PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C07C 337/04, C07D 213/53, 333/22, 307/52, 213/61, 333/28, 207/32, 215/12, 271/06, A01N 47/42

A1

(11) International Publication Number: WO 98/50352

(43) International Publication Date: 12 November 1998 (12.11.98)

(21) International Application Number: PCT/GB98/01234

(22) International Filing Date: 28 April 1998 (28.04.98)

(30) Priority Data:
9708903.1 2 May 1997 (02.05.97) GB

(71) Applicant *(for all designated States except US)*: AGREVO UK LIMITED [GB/GB]; Hauxton, Cambridge CB2 5HU (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: BRIGGS, Geoffrey, Gower [GB/GB]; Chesterford Park, Saffron Walden, Essex CB10 1XL (GB). CORNELL, Clive, Leonard [GB/GB]; Chesterford Park, Saffron Walden, Essex CB10 1XL (GB). THOMAS, Peter, Stanley [GB/GB]; Chesterford Park, Saffron Walden, Essex CB10 1XL (GB).

(74) Agent: SEWELL, Richard, Charles; AgrEvo UK Limited, Patent Dept., Chesterford Park, Saffron Walden, Essex CB10 1XL (GB).

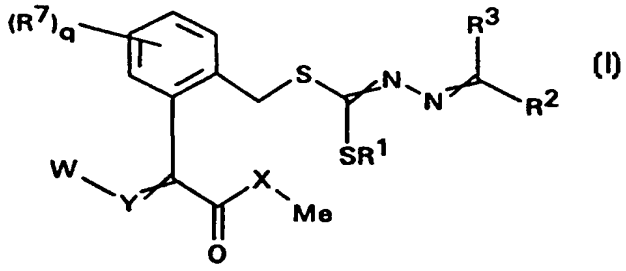
(81) Designated States: AU, BR, CA, CN, CZ, HU, ID, IL, JP, KR, MX, PL, RO, RU, TR, UA, US, VN, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: DITHIOCARBAZONIC ACID DERIVATIVES AS PESTICIDES

(57) Abstract

The invention relates to compounds of general formula (I), wherein X is O or NH; Y is CH or N; W is methyl or methoxy; R^1 and R^2, which may be the same or different, are optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted phenyl or optionally substituted heterocyclyl; R^3 has the same meaning as R^2 or can be hydrogen; or R^2 and R^3 together with the carbon to which they are attached form a 5– to 7–membered heterocyclyl, cycloalkyl or cycloalkenyl group which is optionally substituted; R^7 is alkyl, haloalkyl, alkenyl, alkynyl, cycloalkyl, halogen, cyano, alkoxy, alkylthio, haloalkoxy, and optionally substituted phenyl; and q is 0 to 4.



(I)

FOR THE PURPOSES OF INFORMATION ONLY

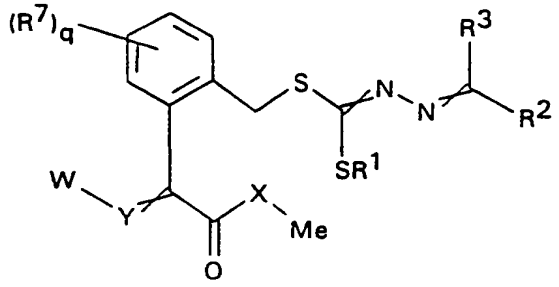
Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

DITHIOCARBAZONIC ACID DERIVATIVES AS PESTICIDES

This invention relates to compounds having pesticidal, especially fungicidal, insecticidal and acaricidal, activity.

The invention provides a compound of general formula I



(I)

wherein

X is O or NH;

Y is CH or N;

W is methyl or methoxy;

R^1 and R^2, which may be the same or different, are optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted phenyl or optionally substituted heterocyclyl;

R^3 has the same meaning as R^2 or can be hydrogen; or

R^2 and R^3 together with the carbon to which they are attached form a 5- to 7-membered heterocyclyl, cycloalkyl or cycloalkenyl group which is optionally substituted;

R^7 is alkyl, haloalkyl, alkenyl, alkynyl, cycloalkyl, halogen, cyano, alkoxy, alkylthio, haloalkoxy, and optionally substituted phenyl; and

q is 0 to 4, preferably 0.

Any alkyl group may be straight or branched and is preferably of 1 to 10 carbon atoms, especially 1 to 7 and particularly 1 to 5. Alkenyl and alkynyl groups are generally of 3 to 6 carbon atoms. Cycloalkyl or cycloalkenyl groups are preferably of 3 to 8 carbon atoms.

Substituents, when present on any alkyl, cycloalkyl, cycloalkenyl, alkenyl or alkynyl moiety include trialkylsilyl, halogen, cyano, optionally substituted alkoxy, optionally substituted alkylthio, optionally substituted haloalkyl, hydroxy, nitro, optionally substituted amino, acyl, acyloxy, optionally substituted phenyl, optionally substituted heterocyclyl, optionally substituted phenoxy, optionally substituted phenylthio, optionally substituted hetercyclyloxy, or optionally substituted heterocyclylthio.

Any cycloalkyl or cycloalkenyl groups may also be substituted by alkyl, alkenyl or alkynyl, all of which may be substituted as described above.

The term heterocyclyl includes both aromatic and non-aromatic heterocyclyl groups. Heterocyclyl groups are generally 5, 6 or 7-membered rings containing up to 4 hetero atoms selected from nitrogen, oxygen and sulfur. Examples of heterocyclyl groups are furyl, thienyl, pyrrolyl, pyrrolinyl, pyrrolidinyl, imidazolyl, dioxolanyl, oxazolyl, thiazolyl, imidazolyl, imidazolinyl, imidazolidinyl, pyrazolyl, pyrazolinyl, pyrazolidinyl, isoxazolyl, isothiazolyl, oxadiazolyl, triazolyl, thiadiazolyl, pyranyl, pyridyl, piperidinyl, dioxanyl, morpholino, dithianyl, thiomorpholino, pyridazinyl, pyrimidinyl, pyrazinyl, piperazinyl, triazinyl, thiazolinyl, benzimidazolyl, tetrazolyl, benzoxazolyl, imidazopyridinyl, benzoxazinyl, benzothiazinyl, oxazolopyridinyl, benzofuranyl, quinolinyl, quinazolinyl, quinoxalinyl, sulfolanyl, dihydroquinazolinyl, benzothiazolyl, phthalimido, benzofuranyl, azepinyl, oxazepinyl, thiazepinyl, diazepinyl and benzodiazepinyl. Heterocyclyl groups may themselves be substituted.

Substituents when present on any phenyl or heterocyclyl group may for example be halogen, trialkylsilyl, CN, NO_2, acyl, O-acyl, SF_5 or a group E^1, OE^1, $-S(O)_nE^1$ or $-(E^1)=NOE^2$, where n is 0, 1 or 2, E^1 and E^2, which may be the same or different, are hydrogen, optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted acyl, optionally substituted phenyl or optionally substituted heterocyclyl. E^1 can also be optionally substituted amino. Alternatively two adjacent groups on the phenyl or heterocyclyl group together with the atoms to which they are attached form a carbocyclic or heterocyclic ring, which may be similarly substituted.

Any amino group may be substituted for example by one or two optionally substituted alkyl or acyl groups, or two substituents can form a ring, preferably a 5 to 7-membered ring, which may be substituted and may contain other hetero atoms, for example morpholine, or piperidine.

The term acyl includes the residue of sulfur and phosphorus-containing acids as well as carboxylic acids. Examples of acyl groups are thus $-C(=O)R^4$, $-C(=O)OR^4$, $-C(=Z)NR^4R^5$, $-C(=O)N(R^4)OR^5$, $-C(=O)ONR^4R^5$, $-C(=O)N(R^4)NR^5R^6$, $-C(=O)SR^4$, $-C(=S)SR^4$, $-S(O)_pR^4$, $-S(O)_2OR^4$, $-S(O)_pR^4R^5$, $-P(=Z)(OR^4)(OR^5)$, $-C(=O)-C(=O)OR^5$, where R^4, R^5 and R^6 which may be the same or different, are hydrogen, optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted phenyl or optionally substituted heterocyclyl or R^5 and R^6 together with the atom(s) to which they are attached can form a ring; p is 1 or 2; and Z is O or S.

In cases where the compounds of the invention exist as the E and Z isomers, the invention includes individual isomers as well as mixtures thereof. In addition, each crossed bond depicted in general formula I represents a double bond having either Z or E stereochemistry.

We have found that compounds where the double bond attached to Y is of E geometry generally provide the highest activity for combating fungi.

In addition, we have found that R^1 is preferably optionally substituted alkyl, especially methyl.

Further we have found that R^3 is preferably hydrogen.

R^2 is preferably optionally substituted alkyl, optionally substituted phenyl or optionally substituted heterocyclyl.

When R^2 is an optionally substituted alkyl group, preferred groups are optionally substituted branched alkyl, particularly optionally substituted tertiary butyl. When substituted, the substituents are preferably halogen, alkyl or optionally substituted phenyl, which when substituted is substituted by alkyl.

When R^2 is an optionally substituted phenyl group or an optionally substituted phenylalkyl group, preferred substituents are alkyl, haloalkyl, halogen, cyano, nitro, haloalkoxy, alkoxy, aryloxy or acyl. Particularly preferred substituents are electron withdrawing groups, especially halogen.

When R^2 is an optionally substituted heterocyclyl group, preferred groups are deactivating aromatic heterocyclyl groups, especially pyridine or pyrimidine. When the heterocyclyl group is substituted, preferred substituents are alkyl, haloalkyl, alkoxy, haloalkoxy, halogen or aryloxy.

Although good activity has been found for all combinations of X, Y and W, we have found particularly good activity when X is NH, Y is N and W is methoxy.

The compounds of the invention have activity as fungicides, especially against fungal diseases of plants, e.g. mildews and particularly barley powdery mildew (*Erysiphe graminis*) and vine downy mildew (*Plasmopara viticola*), rice blast (*Pyricularia oryzae*), cereal eyespot (*Pseudocercosporella herpotrichoides*), rice sheath blight (*Pellicularia sasakii*), grey mould (*Botrytis cinerea*), damping off (*Rhizoctonia solani*), wheat brown rust (*Puccinia recondita*), late tomato or potato blight (*Phytophthora infestans*), apple scab (*Venturia inaequalis*), glume blotch (*Leptosphaeria nodorum*). Other fungi against which the compounds may be active include other powdery mildews, other rusts, and general pathogens of Deuteromycete, Ascomycete, Phycomycete and Basidomycete origin.

The compounds of the invention also have insecticidal, acaricidal and nematicidal activity and are particularly useful in combating a variety of economically important insects, acarids and plant nematodes, including animal ectoparasites and especially Diptera, such as sheep blow-fly, *Lucilia sericata*, and house-flies, *Musca domestica*; Lepidoptera, including *Plutella xylostella*, *Spodoptera littoralis*,

Heliothis armigera and *Pieris brassicae*; Homoptera, including aphids such as *Megoura viciae*; Coleoptera, including corn rootworms (*Diabrotica* spp., e.g. *Diabrotica undecimpunctata*); and spider mites, such as *Tetranychus* spp..

The invention thus also provides a method of combating pests (i.e. fungi, insects, nematodes, acarids and weeds) at a locus infested or liable to be infested therewith, which comprises applying to the locus a compound of formula I.

The invention also provides an agricultural composition comprising a compound of formula I in admixture with an agriculturally acceptable diluent or carrier.

The composition of the invention may of course include more than one compound of the invention.

In addition the composition can comprise one or more additional active ingredients, for example compounds known to possess plant-growth regulant, herbicidal, fungicidal, insecticidal or acaricidal properties. Alternatively the compound of the invention can be used in sequence with the other active ingredient.

The diluent or carrier in the composition of the invention can be a solid or a liquid optionally in association with a surface-active agent, for example a dispersing agent, emulsifying agent or wetting agent. Suitable surface-active agents include anionic compounds such as a carboxylate, for example a metal carboxylate of a long chain fatty acid; an N-acylsarcosinate; mono- or di-esters of phosphoric acid with fatty alcohol ethoxylates or salts of such esters; fatty alcohol sulfates such as sodium dodecyl sulfate, sodium octadecyl sulfate or sodium cetyl sulfate; ethoxylated fatty alcohol sulfates; ethoxylated alkylphenol sulfates; lignin sulfonates; petroleum sulfonates; alkyl-aryl sulfonates such as alkyl-benzene sulfonates or lower alkylnaphthalene sulfonates, e.g. butyl-naphthalene sulfonate; salts of sulfonated naphthalene-formaldehyde condensates; salts of sulfonated phenol-formaldehyde condensates; or more complex sulfonates such as the amide sulfonates, e.g. the sulfonated condensation product of oleic acid and N-methyl taurine or the dialkyl sulfosuccinates, e.g. the sodium sulfonate of dioctyl succinate. Nonionic agents include condensation products of fatty acid esters,

fatty alcohols, fatty acid amides or fatty-alkyl- or alkenyl-substituted phenols with ethylene oxide, fatty esters of polyhydric alcohol ethers, e.g. sorbitan fatty acid esters, condensation products of such esters with ethylene oxide, e.g. polyoxyethylene sorbitan fatty acid esters, block copolymers of ethylene oxide and propylene oxide, acetylenic glycols such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol, or ethoxylated acetylenic glycols.

Examples of a cationic surface-active agent include, for instance, an aliphatic mono-, di-, or polyamine as an acetate, naphthenate or oleate; an oxygen-containing amine such as an amine oxide or polyoxyethylene alkylamine; an amide-linked amine prepared by the condensation of a carboxylic acid with a di- or polyamine; or a quaternary ammonium salt.

The compositions of the invention can take any form known in the art for the formulation of agrochemicals, for example, a solution, a dispersion, an aqueous emulsion, a dusting powder, a seed dressing, a fumigant, a smoke, a dispersible powder, an emulsifiable concentrate or granules. Moreover it can be in a suitable form for direct application or as a concentrate or primary composition which requires dilution with a suitable quantity of water or other diluent before application.

An emulsifiable concentrate comprises a compound of the invention dissolved in a water-immiscible solvent which is formed into an emulsion with water in the presence of an emulsifying agent.

A dusting powder comprises a compound of the invention intimately mixed and ground with a solid pulverulent diluent, for example, kaolin.

A granular solid comprises a compound of the invention associated with similar diluents to those which may be employed in dusting powders, but the mixture is granulated by known methods. Alternatively it comprises the active ingredient absorbed or adsorbed on a pre-granular diluent, for example, Fuller's earth, attapulgite or limestone grit.

Wettable powders, granules or grains usually comprise the active ingredient in admixture with a suitable surfactant and an inert powder diluent such as china clay.

Another suitable concentrate is a flowable suspension concentrate which is formed by grinding the compound with water or other liquid, a wetting agent and a suspending agent.

The concentration of the active ingredient in the composition of the present invention, as applied to plants is preferably within the range of 0.0001 to 1.0 per cent by weight, especially 0.0001 to 0.01 per cent by weight. In a primary composition, the amount of active ingredient can vary widely and can be, for example, from 5 to 95 per cent by weight of the composition.

In the method of the invention the compound is generally applied to seeds, plants or their habitat. Thus, the compound can be applied directly to the soil before, at or after drilling so that the presence of active compound in the soil can control the growth of fungi which may attack seeds. When the soil is treated directly the active compound can be applied in any manner which allows it to be intimately mixed with the soil such as by spraying, by broadcasting a solid form of granules, or by applying the active ingredient at the same time as drilling by inserting it in the same drill as the seeds. A suitable application rate is within the range of from 5 to 1000 g per hectare, more preferably from 10 to 500 g per hectare.

Alternatively the active compound can be applied directly to the plant by, for example, spraying or dusting either at the time when the fungus has begun to appear on the plant or before the appearance of fungus as a protective measure. In both such cases the preferred mode of application is by foliar spraying. It is generally important to obtain good control of fungi in the early stages of plant growth as this is the time when the plant can be most severely damaged. The spray or dust can conveniently contain a pre- or post-emergence herbicide if this is thought necessary. Sometimes, it is practicable to treat the roots of a plant before or during planting, for example, by dipping the roots in a suitable liquid or solid composition. When the active compound is applied directly to the plant a

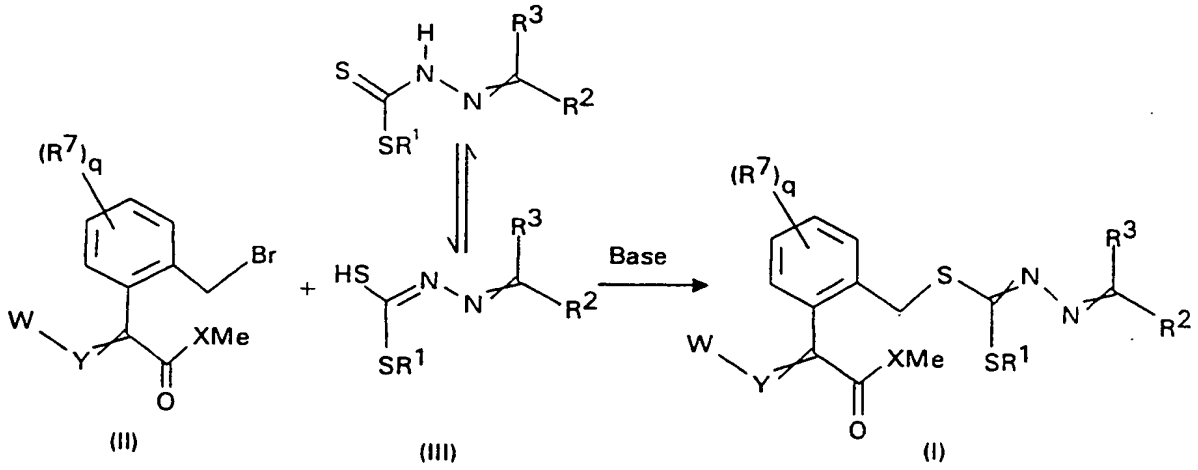
suitable rate of application is from 0.025 to 5 kg per hectare, preferably from 0.05 to 1 kg per hectare.

In addition, the compounds of the invention can be applied to plants or parts thereof which have been genetically modified to exhibit a trait such as fungal and/or herbicidal resistance.

Compounds of the invention may be prepared, in known manner, in a variety of ways.

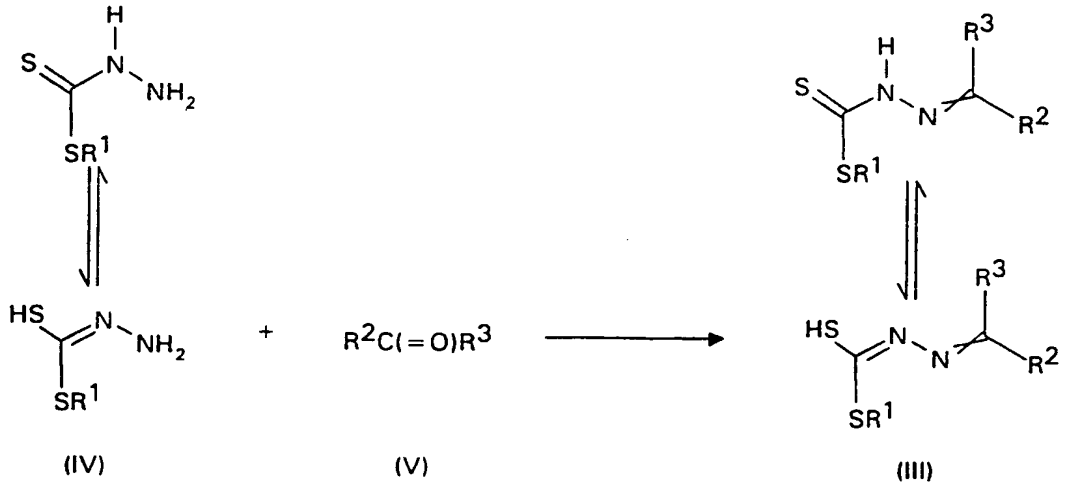
Compounds of general formula I can be prepared by reacting a benzyl bromide of general formula II with a dithiocarbazate of general formula III, in the presence of a suitable base eg sodium hydride, according to the following reaction scheme.

Scheme 1



Intermediates of formula III can be prepared in turn by reacting aldehydes and ketones V with compounds of formula IV. Preferred reaction conditions comprise heating a methanolic solution of IV and V in the presence of a small amount of glacial acetic acid.

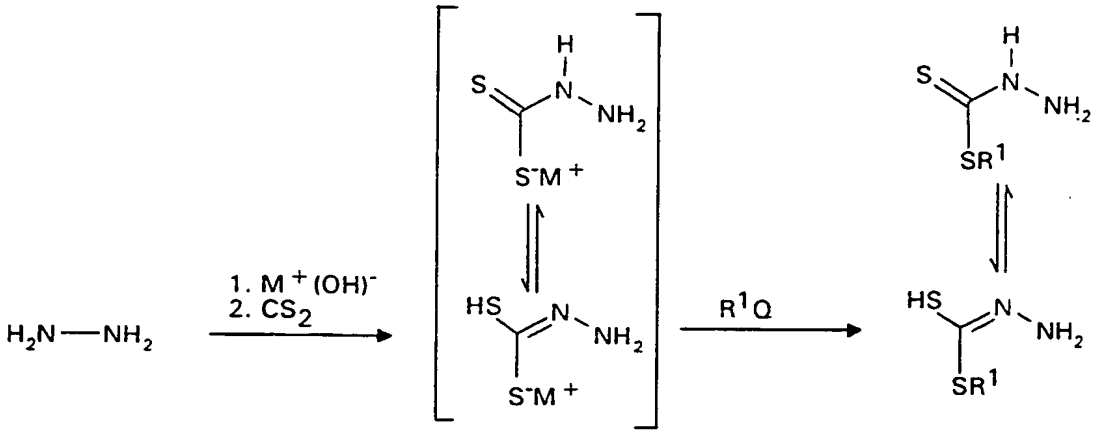
Scheme 2



(IV) (V) (III)

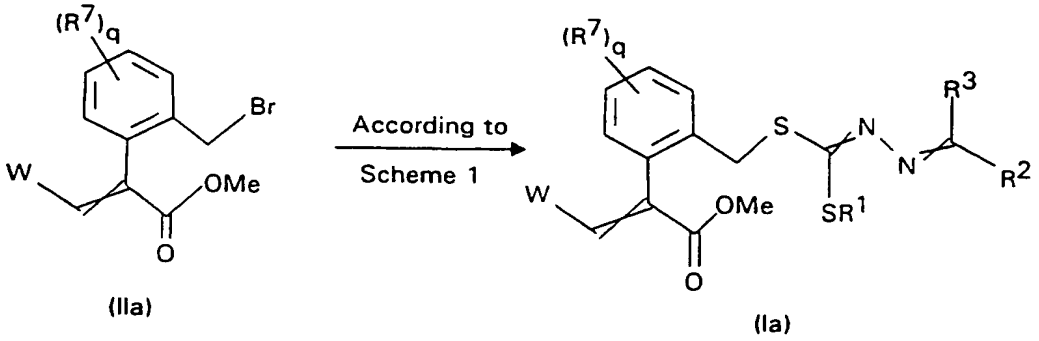
Alkyl dithiocarbazates of formula IV can be prepared by reacting a basic solution of hydrazine hydrate with carbon disulphide followed by addition of a compound of general formula R^1Q where Q is a leaving group, eg halogen, alkyl or aryl sulfonate, alkyl sulfate etc. When R^1 is methyl, Q is preferably methyl sulfate. Preferred bases include metal hydroxides $[M^+(OH)^-]$, such as potassium hydroxide. Alkyl dithiocarbazates IV can either be prepared in one step by addition of R^1Q to the crude reaction mixture or alternatively in two steps by firstly isolating the metallated dithiocarbazate VI as a crystalline solid. When the base is potassium hydroxide the crystalline solid is the mono-potassium salt of dithiocarbazate VI.

Scheme 3



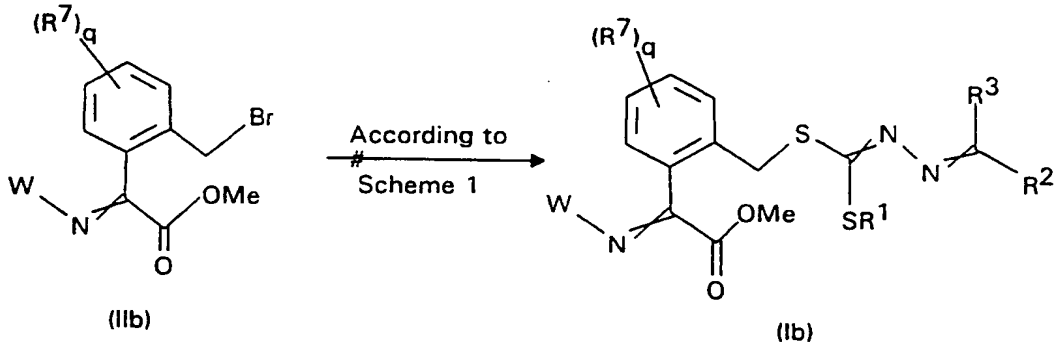
Compounds of formula Ia, i.e. compounds of general formula I where X is O and Y is CH, may be prepared from compounds of formula IIa according to Scheme 5. Compounds of formula IIa may be prepared by methods described in EP 0 299 694.

Scheme 4



Similarly compounds of formula Ib, i.e. compounds of general formula I where X is O and Y is N, may be prepared according to Scheme 6. Compounds of formula IIb may be prepared by methods described in EP 0299694.

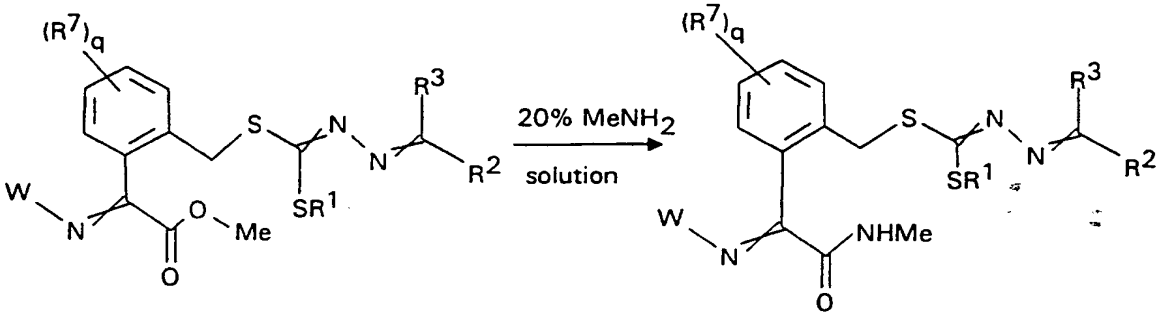
Scheme 5



(IIb) (Ib)

Compounds of formula Ic, i.e. compounds of general formula I where X is NH and Y is N can be prepared by treating compounds of formula Ib with a solution of methylamine in a suitable solvent according to Scheme 7. Preferred reaction conditions comprise stirring with 20% methylamine in methanol at room temperature.

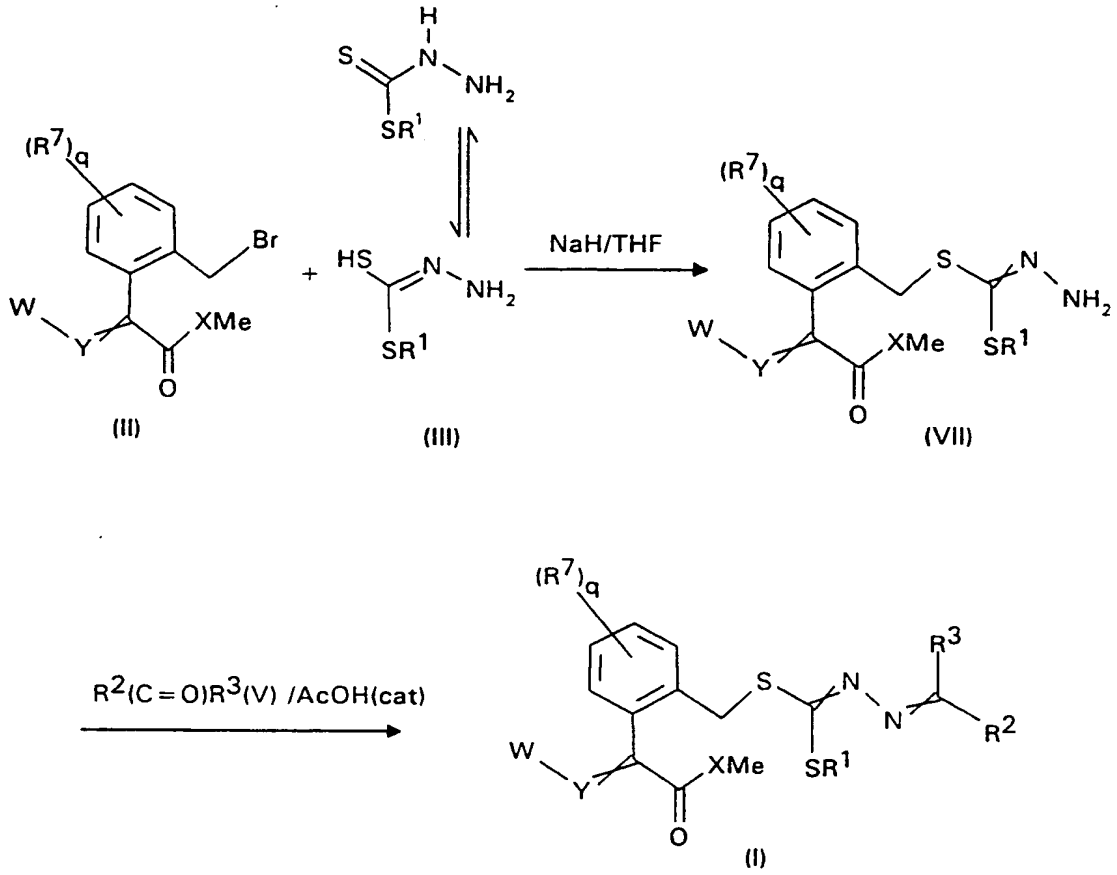
Scheme 6



(Ib) (Ic)

Alternatively to preparing compounds of general formula I by reacting compounds of formula II with compounds of formula III according to Scheme 1, compounds of general formula I can be prepared according to reaction Scheme 8. Preferred reaction conditions for reacting compound II with compound III comprise sodium hydride in tetrahydrofuran. Preferred reaction conditions for reacting compound VII with carbonyl V comprise stirring a methanolic or tetrahydrofuran solution of VII in the presence of a small amount of glacial acetic acid.

Scheme 7



Other methods will be apparent to the chemist skilled in the art as will be the methods for preparing starting materials and intermediates.

The following Examples also make apparent various methods of preparing compounds of the invention as well as starting materials and intermediates of the invention. Structures of isolated novel compounds were confirmed by elemental and/or other appropriate analyses.

Example 1

Methyl 3-methoxy-2-{2-[[1-(3-methylphenyl)ethylidenehydrazono](methylthio) methylthiomethyl]phenyl}acrylate (Compound 1)

Sodium hydride (165 mg of a 60% oil dispersion) was added to a solution of methyl [1-(3-methylphenyl)ethylidene]dithiocarbazate (0.67 g) in dry tetrahydrofuran (20 ml) under an atmosphere of nitrogen. After stirring for 30 minutes, the solution was purged with nitrogen and methyl 3-methoxy-2-[2-(bromomethyl)phenyl]acrylate (see EP 0 299 694 for preparative method) (0.8 g) added. The resulting mixture was stirred for 18 hours, quenched with methanol (0.2 ml) and evaporated under reduced pressure. The residue was taken up in diethyl ether, washed with brine, dried ($MgSO_4$) and concentrated to give an oil. Trituration with diethyl ether/hexane gave the titled product as a mixture of geometric isomers, m.p. 102-5 °C.

Preparation of starting materials

a) Methyl [1-(3-methylphenyl)ethylidene]dithiocarbazate

To a solution of methyl dithiocarbazate (1.22 g) in methanol (10 ml) containing glacial acetic acid (2 drops) was added 3'-methylacetophenone (1.34 g) and the mixture was heated at reflux for 2 hours. The reaction was cooled to room temperature and diluted with diisopropyl ether/hexane 1:1 (8 ml). The resulting solid was filtered and washed with further diisopropyl ether/hexane 1:1 to give the title compound, m.p. 128-130 °C.

b) Methyl dithiocarbazate

Hydrazine hydrate (48.5 ml) was added to a solution of potassium hydroxide (59 g, 85% purity) cooled to 10 °C. The resultant solution was cooled to 5 °C and carbon disulfide (63.5 ml) was added dropwise using efficient stirring and cooling. The resultant mixture was stirred at 0 °C for 1 hour prior to the dropwise addition of dimethyl sulfate (100 ml). The

mixture was stirred at 10 °C for 30 minutes then water (100 ml) was added dropwise followed by further water (250 ml) as a steady stream. The resultant mixture was chilled for 30 minutes and the resulting solid filtered. The solid was washed with water followed by diethyl ether/hexane 1:1 to give the title product, m.p. 80-81 °C.

Example 2

Methyl 3-methoxy-2-{2-[(benzylidenehydrazono)(methylthio)methylthiomethyl] phenyl}acrylate (Compound 6).

To a solution of methyl 3-methoxy-2-{2-[(hydrazono)(methylthio)methylthiomethyl] phenyl}acrylate (0.5 g of major isomer) in dry tetrahydrofuran (10 ml) was added benzaldehyde (0.16 ml), followed by glacial acetic acid (2 drops). The reaction mixture was stirred at room temperature for 1 hour. The solvent was removed and the residue purified by silica gel chromatography using petrol (40-60)/ether as eluents to give the title compound as a 1.38:1 mixture of geometric isomers).

Preparation of starting materials

Methyl 3-methoxy-2-{2-[(hydrazono)(methylthio)methylthiomethyl]phenyl} acrylate

To a solution of methyl dithiocarbazate (1.22 g, starting material from step b) in Example 1) in dry tetrahydrofuran (20 ml) was added, portionwise, sodium hydride (60% dispersion in oil) (400 mg). The solution was stirred at room temperature for 30 minutes before adding dropwise a solution of methyl 3-methoxy-2-[2-(bromomethyl)phenyl]acrylate (EP 0 299 694) (2.86 g) in dry tetrahydrofuran (15 ml). The solution was stirred at room temperature for 56 hours and quenched with a few drops of glacial acetic acid. The reaction mixture was poured onto brine (100 ml) and extracted with diethyl ether (3x50 ml). Organic extracts were combined, washed with water, dried over magnesium sulphate, filtered and evaporated to give a crude product. The crude product was purified by silica gel chromatography using diethyl ether and petrol (b.p. 40-60 °C) as eluents to give title compound as an isomeric mixture; ^{1}H N.M.R. δ(ppm, major isomer) 2.34 (3H, s, CH_3S), 3.74 (3H, s, CH_3O), 3.82 (3H, s, $\underline{CH_3}OOC$), 3.98 (2H, s, $\underline{CH_2}Ar$), 5.60 (2H, s, $N\underline{NH_2}$), 7.08 (1H, m, Ar$\underline{H}$), 7.22 (2H, m,

2xArH), 7.30 (1H, m, Ar-H) and 7.60 (1H, s, MeOCH=), ^{1}H N.M.R. δ(ppm, minor isomer) 2.36 (3H, s, CH_3S), 3.68 (3H, S, CH_3O), 3.80 (3H, s, CH_3OOC), 4.04 (2H, s, CH_2Ar), 5.55 (2H, s N-NH_2), 7.08 (1H, m, Ar-H), 7.24 (2H, m, 2xAr-H) and 7.56 (1H, s, MeOCH=).

Example 3

Methyl (E)-2-(methoxyimino)-2-{2-[(3-methylbenzylidenehydrazono)(methylthio) methylthiomethyl]phenyl}acetate (Compound 165)

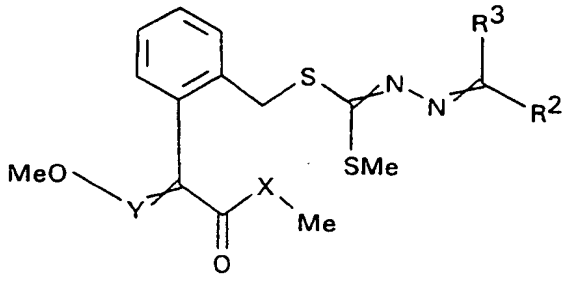
Sodium hydride (150 mg of a 60% oil dispersion) was added to a solution of methyl [1-(3-methylphenyl)ethylidene]dithiocarbazate (0.78 g, starting material from step a) in Example 1) in dry tetrahydrofuran (15 ml). After stirring at room temperature for 15 minutes, a solution containing methyl (E)-2-(methoxyimino)-2-[[2-(bromomethyl)phenyl]acetate EP 0299694 (1.0 g) in dry tetrahydrofuran (5 ml) was added. The solution was stirred at room temperature for 24 hours. The solvent was removed and the residue quenched with water. The mixture was extracted (x3) with ether. The ether extracts were combined, washed with brine, dried over magnesium sulphate, filtered and evaporated to give a crude product which was purified by silica gel chromatography (1:4 ethyl acetate: petrol 40-60) to give the title product, m.p. 108-110°C.

Example 4

(E)-2-(Methoxyimino)-*N*-methyl-2-{2-[(3-methylbenzylidenehydrazono) (methylthio)methylthiomethyl]phenyl}acetamide (Compound 147)

To a solution containing methyl (E) 2-(methoxyimino)-2-[[2-[1-(3-methylphenyl) ethylidinehydroazono] (methylthiomethyl)phenyl] acetate (1.5 g, Compound 165 from Example 3) in tetrahydrofuran (5 ml) and methanol (5 ml) was added 27% w/v solution of methylamine in methanol (3 ml). The solution was allowed to stir at room temperature for 24 hours. Removal of the solvent followed by trituration of the resultant solid with 1:1 petrol 40-60: diethyl ether gave the title product, m.p. 121-125°C.

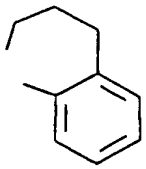
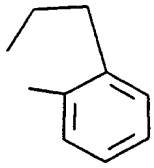
The following compounds of formula Id, i.e. compounds of general formula I where R^1 is methyl and W is methoxy, q is 0, may be prepared by methods analogous to those of Examples 1 to 4. All isolated compounds exist as a mixture of two or more geometric isomers which may equilibrate in solution. It is possible in some cases to separate the mixture into individual geometric isomers. Those instances where this was attempted have been indicated by an asterisk in the Table.



(Id)

Table

Cmp	R^2	R^3	X	Y	m.p./°C
2	Me	4-tolyl	O	CH	117-119
3	H	3-CF_3-phenyl	O	CH	92.5-94.5
4	H	2,6-diCl-phenyl	O	CH	103-106
5*	H	2-CF_3-phenyl	O	CH	113-114.5
6	H	phenyl	O	CH	105-107.5
7	H	4-iPr-phenyl	O	CH	116-118
8	H	4-Me_2N-phenyl	O	CH	162-163.5
9	H	4-MeO-phenyl	O	CH	112-115
10	H	2-CN-phenyl	O	CH	104-106.5
11	H	4-Cl-phenyl	O	CH	119-121
12	H	4-NO_2-phenyl	O	CH	159-160
13	H	2-furyl	O	CH	109.5-111
14	H	2-pyridyl	O	CH	89.5-92
15	H	3-pyridyl	O	CH	110-112
16	H	4-pyridyl	O	CH	99.5-101.5
17	H	4-CF_3O-phenyl	O	CH	98.5-100
18	H	3,4-diMeO-phenyl	O	CH	102-106
19	H	4-tBu-phenyl	O	CH	123-126

Cmp	R^2	R^3	X	Y	m.p./°C
20	H	3-Br-phenyl	O	CH	115.5-117.5
21	H	pentaF-phenyl	O	CH	113-115
22	H	3-NO_2-phenyl	O	CH	134-136
23	H	3,5-xylyl	O	CH	121-123
24	H	3,4-diCl-phenyl	O	CH	100-102
25	H	2,3-diCl-phenyl	O	CH	118-120
26	H	2,5-xylyl	O	CH	106-108
27	H	1-napthyl	O	CH	96.5-98.5
28	H	*N*-Me-3-indolyl	O	CH	183-187
29	H	5-Me-2-pyridyl	O	CH	123-124.5
30			O	CH	101-103
31			O	CH	137-140
32	Me	2-pyridyl	O	CH	96-97.5
33	Me	3-pyridyl	O	CH	99-102
34	Me	4-pyridyl	O	CH	149-150.5
35	CF_3	2-thienyl	O	CH	101-102.5
36	Me	2,4-diMe-5-thiazolyl	O	CH	146-147
37	Me	*N*-Me-2-pyrrolyl	O	CH	102.5-105.5
38	H	4-PhO-phenyl	O	CH	oil
39	H	3-PhO-phenyl	O	CH	oil
40	Me	2-thienyl	O	CH	78-86
41	Ph	phenyl	O	CH	132-136.5
42	Me	phenyl	O	CH	102-104
43*	H	2-thienyl	O	CH	oil (isomeric with 44)
44*	H	2-thienyl	O	CH	oil (isomeric with 43)
45	H	*N*-Me-2-pyrrolyl	O	CH	oil

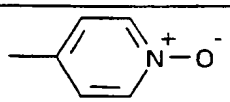
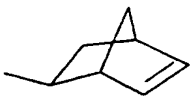
Cmp	R^2	R^3	X	Y	m.p./°C
46	Me	propyl	O	CH	oil
47	CF_3	phenyl	O	CH	oil
48	Me	iso-propyl	O	CH	oil
49	Me	tert-butyl	O	CH	oil
50	Me	cyclopropyl	O	CH	oil
51	$-(CH_2)_4-$		O	CH	oil
52	Et	phenyl	O	CH	oil
53	Pr	phenyl	O	CH	oil
54	Bu	phenyl	O	CH	oil
55	Me	2-Ph-ethyl	O	CH	oil
56	H	2-Ph-ethyl	O	CH	oil
57	H	methyl	O	CH	oil
58	Me	methyl	O	CH	oil
59	Me	2-furyl	O	CH	oil
60	H	ethyl	O	CH	oil
61	H	propyl	O	CH	oil
62	H	tert-butyl	O	CH	oil
63	Me	ethyl	O	CH	oil
64	Me	benzyl	O	CH	oil
65	H	2-MeO-5-pyridyl	O	CH	oil
66	Me	-C(Me)=NOMe	O	CH	oil
67*	H	phenyl	O	CH	oil
68	H	3-CF_3-phenyl	NH	N	55-70
69*	H	2-thienyl	NH	N	oil (isomeric with 70)
70*	H	2-thienyl	NH	N	oil (isomeric with 69)
71*	H	2-thienyl	O	N	oil (isomeric with 72)
72*	H	2-thienyl	O	N	oil (isomeric with 71)
73	H	2-CF_3-phenyl	O	N	131-132
74	H	3-CF_3-phenyl	O	N	oil
75	H	phenyl	O	N	oil

Cmp	R^2	R^3	X	Y	m.p./°C
76	H	4-Cl-phenyl	O	N	138-140
77	H	3,4-diCl-phenyl	O	N	oil
78	H	2-CF_3-phenyl	NH	N	78-85
79	H	phenyl	NH	N	113-114.5
80	H	4-Cl-phenyl	NH	N	126.5-129
81	H	3,4-diCl-phenyl	NH	N	127-129
82	H	3,4-diMeO-phenyl	O	N	108-113
83	H	3-PhO-phenyl	O	N	oil
84	H	pentaF-phenyl	O	N	105-109
85	H	2-pyridyl	O	N	85-89
86	H	3-pyridyl	O	N	oil
87	H	4-pyridyl	O	N	oil
88	Me	3,4-diMeO-phenyl	NH	N	124-128
89	H	3-PhO-phenyl	NH	N	oil
90	H	pentaF-phenyl	NH	N	134-137
91	H	tert-butyl	O	N	80-81
92	H	2-MeO-5-pyridyl	O	N	165-170
93	Me	-C(Me)=NOMe	O	N	93-94
94	H	3-pyridyl	NH	N	oil
95	H	2-pyridyl	NH	N	51-56
96	Me	-C(Me)=NOMe	NH	N	102-105
97	H	4-pyridyl	NH	N	59-65
98	H	tert-butyl	NH	N	87-90
99	H	2-MeO-5-pyridyl	NH	N	57-60
100	H	2-quinolinyl	O	N	128-130
101	H	4-iPr-phenyl	O	N	oil
102	H	4-MeO-phenyl	O	N	133-135
103	Ph	phenyl	O	N	142-144
104	H	4-CF_3O-phenyl	O	N	oil
105	H	3,5-xylyl	O	N	oil
106	H	2,3-diCl-phenyl	O	N	130-132

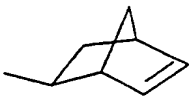
Cmp	R^2	R^3	X	Y	m.p./°C
107	H	2,5-xylyl	O	N	oil
108	H	1-napthyl	O	N	oil
109	Et	phenyl	O	N	oil
110	Pr	phenyl	O	N	oil
111	Me	2-Ph-ethyl	O	N	oil
112	H	2-quinolinyl	NH	N	136-138
113	H	4-iPr-phenyl	NH	N	128-136
114	H	4-MeO-phenyl	NH	N	130-132
115	H	4-CF_3O-phenyl	NH	N	98-100
116	H	3,5-xylyl	NH	N	94-96
117	H	2,5-xylyl	NH	N	108-110
118	H	2,6-diCl-phenyl	O	N	133-135
119	H	3-Br-phenyl	O	N	83-86
120	H	4-Br-phenyl	O	N	133-135
121	Et	4-Cl-phenyl	O	N	86-89
122	H	2-F-phenyl	O	N	87-89
123	H	4-F-phenyl	O	N	100-103
124	H	2,4-diF-phenyl	O	N	103-105
125	Me	4-F-phenyl	O	N	106-107
126	H	3-Br-phenyl	NH	N	133-135
127	H	4-Br-phenyl	NH	N	121-123
128	Et	phenyl	NH	N	104-108
129	H	2-F-phenyl	NH	N	107-110
130	H	4-F-phenyl	NH	N	128-130
131	H	2,4-diF-phenyl	NH	N	131-133
132	Me	4-F-phenyl	NH	N	100-103
133	Me	3-pyridyl	O	N	99-100
134	H	1-napthyl	NH	N	96-99
135	H	2,3-diCl-phenyl	NH	N	125-128
136	Et	phenyl	NH	N	106-108
137	Pr	phenyl	NH	N	121-124
138	Me	3-pyridyl	NH	N	105-108

Cmp	R^2	R^3	X	Y	m.p./°C
139	H	2,6-diCl-phenyl	NH	N	109-112
140	H	3-F-phenyl	NH	N	100-102
141	H	3,4-diF-phenyl	NH	N	103-106
142	H	2,6-diF-phenyl	NH	N	77-79
143	Me	2,4-diF-phenyl	NH	N	75-79
144	H	2,4,5-triF-phenyl	NH	N	123-126
145	H	2-tolyl	NH	N	118-120
146	Me	4-Cl-phenyl	NH	N	118-120
147	H	3-tolyl	NH	N	79-84
148	Me	2-Ph-ethyl	NH	N	104-107
149	Me	*N*-Me-2-pyrrolyl	NH	N	127-130
150	H	4-tolyl	NH	N	121-125
151	Me	4-tolyl	NH	N	140-142
152	H	4-$MeSO_2$-phenyl	NH	N	143-145
153	Me	4-$MeSO_2$-phenyl	NH	N	oil
154	Me	4-tolyl	O	N	100-104
155	H	4-tolyl	O	N	111-113
156	H	3-F-phenyl	O	N	111-113
157	H	3,4-diF-phenyl	O	N	117-119
158	H	4-$MeSO_2$-phenyl	O	N	oil
159	H	2,6-diF-phenyl	O	N	109-110
160	Me	4-$MeSO_2$-phenyl	O	N	126-128
161	Me	2,4-diF-phenyl	O	N	91-92
162	H	2,4,5-triF-phenyl	O	N	109-110
163	H	2-tolyl	O	N	102-104
164	Me	4-Cl-phenyl	O	N	102-103
165	H	3-tolyl	O	N	108-110
166	H	4-Me_2N-phenyl	NH	N	138-140
167	H	2-CN-phenyl	NH	N	132-134
168	Me	methyl	NH	N	oil
169	Me	phenyl	NH	N	118-119

Cmp	R^2	R^3	X	Y	m.p./°C
170	Me	tert-butyl	NH	N	oil
171	Me	2-pyridyl	NH	N	87-89
172	Me	4-pyridyl	NH	N	189-191
173	H	1,3-thiazol-2-yl	NH	N	166-169
174	H	3-quinolinyl	NH	N	145-147
175	H	2-Me-prop-1-enyl	NH	N	oil
176	H	5-Me-2-thienyl	NH	N	oil
177	H	4-Br-2-thienyl	NH	N	oil
178	H	5-Br-2-thienyl	NH	N	oil
179	Me	3-Me-2-thienyl	NH	N	oil
180	Me	5-Cl-2-thienyl	NH	N	oil
181	Et	2-thienyl	NH	N	112-115
182	H	4-tBu-phenyl	NH	N	135-139
183	H	4-PhO-phenyl	NH	N	102-105
184	H	3-thienyl	NH	N	oil
185	H	*N*-Me-2-pyrrolyl	NH	N	118-121
186	$-(CH_2)_2-S-CH_2-$		NH	N	oil
187	$-(CH_2)_2-S-(CH_2)_2-$		NH	N	oil
188	H	5-Me-2-furyl	NH	N	oil
189	H	2-benzo[b]furyl	NH	N	116-120
190	H	5-Et-2-furyl	NH	N	oil
191	H	4,5-diMe-2-furyl	NH	N	oil
192	H	5-Br-2-furyl	NH	N	oil
193	H	cyclohexyl	NH	N	oil
194	H	cyclohex-3-enyl	NH	N	oil
195	H	1-Me-2-Ph-vinyl	NH	N	121-124
196	H	4-Me_2N-phenyl	O	N	oil
197	H	2-CN-phenyl	O	N	oil
198	Me	methyl	O	N	oil
199	Me	phenyl	O	N	oil
200	Me	tert-butyl	O	N	oil

Cmp	R^2	R^3	X	Y	m.p./°C
201	Me	2-pyridyl	O	N	oil
202	Me	4-pyridyl	O	N	oil
203	H	1,3-thiazol-2-yl	O	N	oil
204	H	3-quinolinyl	O	N	oil
205	H	3-Cl-5-CF_3-2-pyridyl	O	N	121-123
206	H		O	N	163.5-165
207	H	2-Me-prop-1-enyl	O	N	oil
208	Me	α,α-diMe-4-Cl-benzyl	NH	N	138-139
209	Me	3-tolyl	NH	N	98-100
210	H	3-furyl	NH	N	112-114
211	Me	2,5-diMe-3-furyl	NH	N	120-121
212	H	5-Cl-2-thienyl	NH	N	121-123
213	H	α-Me-benzyl	NH	N	oil
214	H	1-CF_3-ethyl	NH	N	oil
215	H	2-(4-MeO-phenyl)vinyl	NH	N	oil
216	-$(CH_2)_2$-O-$(CH_2)_2$-		NH	N	oil
217	H	1-Et-propyl	NH	N	oil
218	H		NH	N	oil
219	H	1,1-diMe-allyl	NH	N	oil
220	H	1-Me-3-Ph-butyl	NH	N	oil
221	Me	5-Me-2-thienyl	O	N	oil
222	H	5-Me-2-thienyl	O	N	oil
223	H	3-thienyl	O	N	oil
224	H	4-Br-2-thienyl	O	N	oil
225	H	5-Br-2-thienyl	O	N	oil
226	H	4-tBu-phenyl	O	N	oil
227	Me	5-Cl-2-thienyl	O	N	oil
228	-$(CH_2)_2$-S-CH_2--		O	N	oil

Cmp	R^2	R^3	X	Y	m.p./°C
2291		$-(CH_2)_2-S-(CH_2)_2-$	O	N	oil
230	H	3-furyl	O	N	oil
231	H	5-Me-2-furyl	O	N	oil
232	H	2-benzo[b]furyl	O	N	oil
233	H	5-Et-2-furyl	O	N	oil
234	H	2,5-diMe-3-furyl	O	N	oil
235	H	4,5-diMe-2-furyl	O	N	oil
236	H	5-Br-2-furyl	O	N	oil
237	H	cyclohexyl	O	N	oil
238	H	cyclohex-3-enyl	O	N	oil
239	H	isopropyl	NH	N	oil
240	H	3-(4-tBu-phenoxy)phenyl	NH	N	126-130
241	H	3-(3-CF_3-phenoxy)phenyl	NH	N	108-110
242	H	3-hexyloxyphenyl	NH	N	oil
243	H	3-(1,1,2,2-tetraF-ethoxy)phenyl	NH	N	oil
244	H	3-(3,4-diCl-phenoxy)phenyl	NH	N	oil
245	H	2-Ph-vinyl	NH	N	oil
246	Me	*N*-Me-2-pyrrolyl	O	N	102-104
247	H	iso-propyl	O	N	oil
248	H	3-(4-tBu-phenoxy)phenyl	O	N	oil
249	H	3-(3-CF_3-phenoxy)phenyl	O	N	oil
250	H	3-Hexyloxy-phenyl	O	N	oil
251	H	3-(3,4-diCl-phenoxy)phenyl	O	N	oil
252	H	2-Ph-vinyl	O	N	118-121
253	H	3-(1,1,2,2-tetraF-ethoxy)phenyl	O	N	oil
254	H	1-Ph-ethyl	O	N	oil
255	H	1-CF_3-ethyl	O	N	oil

Cmp	R^2	R^3	X	Y	m.p./°C
256	H	2-(4-MeO-phenyl)vinyl	O	N	oil
257		-$(CH_2)_2$-O-$(CH_2)_2$--	O	N	oil
258	H	1-Et-propyl	O	N	oil
259	H		O	N	oil
260	Me	α,α-diMe-4-Cl-benzyl	O	N	oil
261	H	1,1-diMe-allyl	O	N	oil
262	H	1-Me-4-Ph-butyl	O	N	oil
263	Me	3-tolyl	O	N	oil
264	H	4-PhO-phenyl	O	N	oil
265	H	*N*-Me-2-pyrrolyl	O	N	oil
266	H	6-Me-2-pyridyl	O	N	oil
267	Me	2-thienyl	O	N	oil
268	H	5-NO_2-2-furyl	O	N	120-123
269	H	5-NO_2-2-furyl	NH	N	133-136
270	H	4-CF_3-phenyl	O	N	111-112
271	H	4-MeOC(=O)-phenyl	O	N	125-127
272	H	3-CF_3-4-F-phenyl	O	N	oil
273	H	2-MeO-pyrimidin-5-yl	O	N	86-89
274	H	4-CF_3-phenyl	NH	N	104-106
275	H	3-CF_3-4-F-phenyl	NH	N	80-84
276	H	4-CN-phenyl	O	N	173-175
277	H	4-CN-phenyl	NH	N	124-128
278	H	3-NO_2-phenyl	O	N	133.5-135.5
279	H	3-NO_2-phenyl	NH	N	141-144
280	H	4-NO_2-phenyl	O	N	174-176
281	H	4-NO_2-phenyl	NH	N	177-178
282	H	3-Cl-4-NO_2-phenyl	NH	N	
283	H	2-NO_2-6-Cl-phenyl	NH	N	

Cmp	R^2	R^3	X	Y	m.p./°C
284	H	2-CF_3O-phenyl	NH	N	
285	H	4-F-3-NO_2-phenyl	NH	N	
286	H	2-CO_2Me-phenyl	NH	N	
287	H	2-$CONMe_2$-phenyl	NH	N	
288	H	2-NO_2-phenyl	NH	N	
289	H	3-CN-phenyl	NH	N	
290	H	2-F-5-NO_2-phenyl	NH	N	
291	H	4-Cl-3-NO_2-phenyl	NH	N	
292	H	3-Cl-6-NO_2-phenyl	NH	N	
293	H	4-(1,2,4-triazolyl)-phenyl	NH	N	
294	H	4-(1-imidazolyl)-phenyl	NH	N	
295	H	3-(1,2,4-oxadiazol-3-yl)-phenyl	NH	N	
296	H	3-(5-Me-1,2,4-oxadiazol-3-yl)phenyl	NH	N	
297	H	4-(1,2,4-oxadiazol-3-yl)phenyl	NH	N	
298	H	4-(5-Me-1,2,4-oxa-diazol-3-yl)phenyl	NH	N	
299	H	3-F-4-MeO-phenyl	NH	N	
300	H	4-CHF_2O-phenyl	NH	N	
301	H	4-CHF_2CF_2O-phenyl	NH	N	
302	H	4-MeON=C-phenyl	NH	N	
303	H	3-MeON=C-phenyl	NH	N	
304	H	4-Me_2NSO_2-phenyl	NH	N	
305	H	2-Cl-3-pyridyl	NH	N	
306	H	6-Cl-2-pyridyl	NH	N	
307	H	6-Cl-3-pyridyl	NH	N	
308	H	6-F-3-pyridyl	NH	N	
309	H	6-Me-3-pyridyl	NH	N	

Cmp	R^2	R^3	X	Y	m.p./°C
310	H	2-Me-3-pyridyl	NH	N	
311	H	5,6-diCl-3-pyridyl	NH	N	
312	H	2,6-diCl-3-pyridyl	NH	N	
313	H	3-Cl-5-CF_3-2-pyridyl	NH	N	
314	H	6-CHF_2O-3-pyridyl	NH	N	
315	H	5-Cl-pyrimidin-2-yl	NH	N	
316	H	2-MeO-pyrimidin-5-yl	NH	N	
317	H	2-F-pyrimidin-5-yl	NH	N	
318	H	2-Cl-primidin-5-yl	NH	N	
319	H	2-Me-pyrimidin-5-yl	NH	N	
320	H	2-Ph-pyrimidin-5-yl	NH	N	
321	H	2-NMe_2-pyrimidin-5-yl	NH	N	
322	H	2-MeNH-pyrimidin-5-yl	NH	N	

The ^{1}H N.M.R. data of those compounds in Table I which did not possess discrete melting points at room temperature are presented below.

Compound 38

^{1}H N.M.R. δ(ppm) 2.42 (3H, s, $\underline{CH_3}S$), 2.55 (3H, s, $\underline{CH_3}S$), 3.68 (3H, s, $\underline{CH_3}O$), 3.70 (3H, s, $\underline{CH_3}O$), 3.83 (3H, s, $\underline{CH_3}OOC$), 3.85 (3H, s, $\underline{CH_3}OOC$), 4.18 (2H, s, $\underline{CH_2}Ar$), 4.35 (2H, s, $\underline{CH_2}Ar$), 6.95-7.78 (26H, m, 2x13 Ar-$\underline{H}$), 7.60 (2H, m, 2x=$\underline{CH}OCH_3$), 8.25 (1H, s, Ar$\underline{CH}$=N) and (1H, s, Ar$\underline{CH}$=N).

Compound 39

^{1}H N.M.R. δ(ppm) 2.42 (3H, s, $\underline{CH_3}$), 2.55 (3H, s, $\underline{CH_3}S$), 3,66 (3H, s, $\underline{CH_3}O$), 3.70 (3H, s, $\underline{CH_3}O$), 3.80 (3H, s, $\underline{CH_3}OOC$), 3.84 (3H, s, CH_3OOC), 4.15 (2H, s, $\underline{CH_2}Ar$, 4.32 (2H, S, $\underline{CH_2}Ar$), 6.96-7.55 (26h, m, 2 x 13 Ar-$\underline{H}$), 7.6 (2H, m, 2x=$\underline{CH}OCH_3$), 8.26 (1H, s, Ar$\underline{CH}$=N) and 8.32 (1H, s, Ar$\underline{CH}$=N).

Compound 43

^{1}H N.M.R. δ(ppm) 2.44 (3H, s, CH_3S), 2.54 (3H, s, CH_3S), 3.66 (6H, m, 2xCH_3O), 3.82 (6H, m, 2xCH_3OOC), 4.20 (2H, s, CH_2Ar), 4,36 (2H, s, CH_2Ar), 7.02-7.5 (14H, m, 2x7Ar-H/Het-H), 7.6 (2H, m, 2x-$CHOCH_3$), 8.42 (1H, s, ArCH=N) and 8.48 (1H, s, ArCH=N).

Compound 44

^{1}H N.M.R. δ(ppm) 2.46 (3H, s, CH_3S), 2.74 (3H, s, CH_3S), 3.64 (6H, m, 2xCH_3O), 3.78 (3H, s, CH_3OOC), 3.82 (3H, s, CH_3OOC), 4.20 (2H, s, CH_2O Ar), 4.58 (2H, s, CH_2Ar), 7.06-7.56 (14H, m, 2x7Ar-H/Het-H), 7.6 (2H, m, 2x=$CHOCH_3$), 8.00 (1H, s, ArCH=N) and 8.04 (1H, s, ArCH=N).

Compound 45

^{1}H N.M.R. δ(ppm) 2.42 (3H, s, CH_3S), 2.55 (3H, s, CH_3S), 3.62 (3H, s, CH_3O), 3.64 (3H, s, CH_3O), 3.80 (3H, s, CH_3N), 3.82 (3H, s, CH_3N), 3.82 (3H, s, CH_3N), 3.9 (3H, s, CH_3OOC), 3.98 (3H, s, CH_3OOC), 4.16 (2H, s, CH_2Ar), 4.34 (2H, s, CH_2Ar), 6.14 (2H, m, 2xHet-H), 6.54 (2H, m, 2xHet-H), 6.76 (2H, m, 2xHet-H), 7.14 (2H, m, 2xAr-H), 7.28 (4H, m, 2xAr-H), 7.56 (2H, m, 2xAr-H), 7.6 (2H, m, 2x=$CHOCH_3$), 8.24 (1H, s, ArCH=N) and 8.30 (1H, s, ArCH=N).

Compound 46

^{1}H N.M.R. δ(ppm) 0.92 (9H, m, CH_3CH_2), 1.56 (6H, m, 3xCH_2CH_3), 1.94 (6H, m, 2xCH_3C=), 2.04 (3H, s, CH_3C=), 2.16 (6H, m, 3 x CH_2CH_2), 2.40 (6H, m, 2 x CH_3S), 2.48 (3H, s, CH_3C), 3.68 (9H, s, 3xCH_3O), 3.82 (9H, m, 3xCH_3OOC), 4.14 (2H, s, CH_2Ar), 4.26 (4H, m, 2xCH_2Ar), 7.12 (3H, m, 3xAr-H), 7.24 (6H, m, 3x2Ar-H), 7.46 (3H, m, 3xAr-H) and 7.58 (3H, m, 3x=CH_3OCH_3).

Compound 47

^{1}H N.M.R. δ(ppm) 2.06 (3H, s, CH_3S), 2.44 (3H, s, CH_3S), 3.62 (3H, s, CH_3O), 3.68 (3H, s, CH_3O), 3.70 (3H, s, CH_3OOC), 3.82 (3H, s, CH_3OOC), 4.04 (2H, s, CH_2Ar), 4.38 (2H, s, CH_2Ar), 7.02-7.5 (18H, m, 2x9Ar-H) and 7.62 (2H, m, 2x$CHOCH_3$).

Compound 48

^{1}H N.M.R. δ(ppm) 1.10 (12H, m, 2x$CH(CH_3)_2$), 1.90 (6H, m, 2xH_3-C=), 2.38 (3H, s, CH_3S), 2.46 (3H, s, CH_3S), 2.56 (2H, m, 2x$CH(CH_3)_2$), 3.68 (6H, s, 2xCH_3O), 3.80 (6H, m, 2xCH_3OOC), 4.14 (2H, s, CH_2Ar), 4.24 (2H, s, CH_2Ar), 7.10 (2H, m, 2 x Ar-H), 7.26 (4H, m, 2xAr-H), 7.48 (2H, m, 2xAr-H) and 7.60 (2H, m, 2x=$CHOCH_3$).

Compound 49

^{1}H N.M.R. δ(ppm) 1.12 (9H, s, $C(CH_3)_3$), 1.92 (6H, m, 2xCH_3-C=), 2.38 (3H, s, CH_3S), 2.50 (3H, s, CH_3S), 2.66 (6H, s, 2xCH_3O), 2.82 (6H, s, CH_3OOC), 4.14 (2H, s, CH_2Ar), 4.26 (2H, s, CH_2Ar), 7.10 (2H, m, 2xAr-H), 7,28 (4H, m, 2x2Ar-H), 7.5 (2H, m, 2xAr-H) and 7.58 (2H, m, 2x=$CHOCH_3$).

Compound 50

^{1}H N.M.R. δ(ppm) 0.90 (16H, m, 4xCH_2CH_2), 1.66 (4H, m, 4x$CHCH_2$), 1.84 (12H, m, 4xCH_3C=), 2.38 (6H, m, 2xCH_3S), 2.50 (6H, m, CH_3S), 3.66 (12H, m, 4xCH_3O), 3.82 (12H, m, 4xCH_3OOC), 4.14 (4H, m, 2xCH_2Ar), 4.26 (4H, m, 2xCH_2Ar), 7.10 (4H, m, 4xAr-H), 7.28 (8H, m, 4x2Ar-H), 7.46 (4H, m, 4xAr-H) and 7.58 (4H, m, 4x=$CHOCH_3$).

Compound 51

^{1}H N.M.R. δ(ppm) 1.76 (8H, m, 2xCH_2CH_2), 2.40 (3H, s, CH_3S), 2.44 (3H, s, CH_3S), 2.46 (8H, m, 4x=CCH_2), 3.66 (6H, s, 2xCH_3O), 3.82 (6H, s, 2xCH_3OOC), 4.15 (2H, s, CH_2Ar), 4.26 (2H, CH_2Ar), 7.10 (2H, m, 2xAr-H), 7.24 (4H, m, 2x2Ar-H), 7.50 (2H, m, 2xAr-H) and 7.60 (2H, m, 2x$CHOOCH_3$).

Compound 52

^{1}H N.M.R. δ(ppm) 1.14 (6H, m, 2xCH_3CH_2), 2.44 (3H, s, CH_3S), 2.58 (3H, s, CH_3S), 2.94 (4H, m, 2x2CH_2CH_3), 3.68 (3H, s, CH_3O), 3.70 (3H, s, CH_3O), 3.80 (3H, s, CH_3OOC), 3.82 (3H, s, CH_3OOC), 4.18 (2H, s, CH_2Ar), 4.38 (2H, s, CH_2Ar), 7.14 (2H, m, 2xAr-H), 7.32 (10H, m, 2x5Ar-H), 7.54 (2H, m, 2xAr-H), 7.60 (2H, m, 2x=$CHOCH_3$) and 7.84 (4H, m, 2x2Ar-H).

Compound 53

^{1}H N.M.R. δ(ppm) 0.94 (6H, m, 2xCH_3CH_2), 1.58 (4H, m, 2xCH_2CH_3), 2.44 (3H, s, CH_3S), 2.58 (3H, s, CH_3S), 2.90 (4H, m, 2x=CCH_2), 3.64 (3H, s, CH_3O), 3.68 (3H, s, CH_3O), 3.80 (3H, s, CH_3OOC), 3.84 (3H, s, CH_3OOC), 4.18 (2H, s, CH_2Ar), 4.35 (2H, s, CH_2Ar), 7.14 (2H, m, 2xAr-H), 7.34 (10H, m, 2x5Ar-H), 7.54 (2H, m, 2xAr-H), 7.62 (2H, m, 2x=$CHOCH_3$) and 7.84 (4H, m, 2x2Ar-H).

Compound 54

^{1}H N.M.R. δ(ppm) 0.9 (6H, m, 2xCH_3CH_2), 1.34 (4H, m, 2xCH_2CH_3), 1.52 (4H, m, 2x$CH_2CH_2CH_3$), 2.44 (3H, s, CH_3S), 2.56 (3H, s, CH_3O), 2.92 (4H, m, 2x=CCH_3), 3.66 (3H, s, CH_3O), 3.68 (3H, s, CH_3O), 3.80 (3H, s, CH_3OOC), 3.84 (3H, s, CH_3OOC), 4.18 (2H, s, CH_2Ar), 4.35 (2H, s, CH_2Ar), 7.14 (2H, m, 2 x Ar-H), 7.34 (10H, m, 2x4Ar-H), 7.60 (2H, m, 2x=$CHOCH_3$) and 7.84 (4H, m, 2x2Ar-H).

Compound 55

^{1}H N.M.R. δ(ppm) 1.98 (9H, m, 3x=CHC$\underline{H}_3$), 2.40 (6H, m, 2xC$\underline{H}_3$S), 2.50 (3H, s, C$\underline{H}_3$S), 2.55-2.94 (12H, m, 3x2C$\underline{H}_2$), 3.62 (3H, s, C$\underline{H}_3$O), 3.68 (6H, m, 2C$\underline{H}_3$O), 3.72 (3H, s, C$\underline{H}_3$OOC), 3.84 (6H, m, 2xC$\underline{H}_3$OOC), 4.18 (2H, s, C$\underline{H}_2$Ar), 4.25 (4H, m, 2xC$\underline{H}_2$Ar), 7.68-7.34 (24H, m, 3x8Ar-$\underline{H}$), 7.50 (3H, m, 3xAr-$\underline{H}$) and 7.58 (3H, m, 3x=C$\underline{H}$OCH$_3$).

Compound 56

^{1}H N.M.R. δ(ppm) 2.40 (6H, m, 2xC$\underline{H}_3$S), 2.46 (3H, s, C$\underline{H}_3$S), 2.62-2.90 (12H, m, 3x2C$\underline{H}_2$), 3.64 (3H, s, C$\underline{H}_3$O), 3.68 (6H, m, 2xC$\underline{H}_3$O), 3.76 (3H, s, C$\underline{H}_3$OOC), 4.02 (6H, m, 2xC$\underline{H}_3$OOC), 4.16 (2H, s, C$\underline{H}_2$Ar), 4.26 (4H, m, 2xC$\underline{H}_2$Ar), 7.10-7.34 (24H, m, 3x8Ar-$\underline{H}$), 7.50 (3H, m, 3xAr-$\underline{H}$), 7.58 (3H, m, 3x=C$\underline{H}$OCH$_3$) and 7.76 (3H, m, 3xN=C$\underline{H}$CH$_2$).

Compound 57

^{1}H N.M.R. δ(ppm) 1.98 (6H, m, 2x=CC$\underline{H}_3$), 2.04 (6H, m, 2x=CC$\underline{H}_3$), 2.40 (6H, m, 2xC$\underline{H}_3$S), 2.48 (6H, m, 2xC$\underline{H}_3$S), 3.68 (12H, s, 4xC$\underline{H}_3$O), 4.02 (12H, m, 4xC$\underline{H}_3$OOC), 4.15 (2H, s, C$\underline{H}_2$Ar), 4.24 (2H, s, C$\underline{H}_2$Ar), 4.30 (2H, s, C$\underline{H}_2$Ar), 4.44 (2H, s, C$\underline{H}_2$Ar), 7.12 (4H, m, 4xAr-$\underline{H}$), 7.16 (8H, m, 2x2Ar-$\underline{H}$), 7.48 (2H, m, 4xAr-$\underline{H}$), 7.58 (4H, m, 4x=C$\underline{H}$OCH$_3$) and 7.75 (4H, m, 4xN=C$\underline{H}$CH$_3$).

Compound 58

^{1}H N.M.R. δ(ppm) 1.98 (9H, m, 3x=CC$\underline{H}_3$), 2.06 (3H, s, =CC$\underline{H}_3$), 2.40 (3H, s, C$\underline{H}_3$S), 3.80 (3H, s, C$\underline{H}_3$S), 3.68 (6H, s, 2xC$\underline{H}_3$O), 3.80 (6H, m, 2xC$\underline{H}_3$OOC), 4.15 (2H, s, C$\underline{H}_2$Ar), 4.28 (2H, s, C$\underline{H}_2$Ar), 7.14 (2H, m, 2xAr-$\underline{H}$), 7.26 (4H, m, 2x2Ar-$\underline{H}$), 7.48 (2H, m, 2xAr-$\underline{H}$) and 7.58 (2H, m, 2x=C$\underline{H}$OCH$_3$).

Compound 59

^{1}H N.M.R. δ(ppm) 2.28 (3H, s, $CH_3C=$), 2,36 (3H, s, $CH_3C=$), 2.42 (6H, m, $CH_3C=$ and CH_3S), 2.55 (3H, s, CH_3S), 2.60 (3H, s, CH_3S), 3.68 (9H, m, 3xCH_3O), 3.76 (3H, s, CH_3OOC), 4.02 (6H, m, 2xCH_3OOC), 4.16 (2H, s, CH_2Ar), 4.34 (4H, m, 2xCH_2Ar), 6.42 (3H, m, 3xHet-H), 6.82 (3H, m, 3xHet-H), 7.13 (3H, m, 3xAr-H), 7.26 (6H, m, 3x2 Ar-H), 7.48 (6H, m, 3xArH/3xHet-H) and 7.60 (3H, m, 3x=$CHOCH_3$).

Compound 60

^{1}H N.M.R. δ(ppm) 1.12 (9H, m, 3xCH_3CH_2), 2.28-2.50 (6H, m, 3xCH_2CH_3), 2.38 (3H, s, CH_3S), 2.42 (3H, s, CH_3S), 2.45 (3H, s, CH_3S), 3.66 (9H, s, 3xCH_3O), 3.82 (9H, m, 3xCH_3OOC), 7.10 (3H, m, 3xAr-H), 7.26 (6H, m, 3x2Ar-H), 7.46 (3H, m, 3xAr-H), 7.58 (3H, m, 3x$CHOCH_3$) and 7.72 (3H, m, N=$CHCH_2$).

Compound 61

^{1}H N.M.R. δ(ppm) 0.96 (9H, m, 3xCH_3CH_2), 1.60 (6H, m, 3xCH_3CH_2), 2.35 (6H, m, 3x$CH_2CH_2CH_3$), 2.40 (3H, s, CH_3S), 2.44 (3H, s, CH_3S), 2.46 (3H, s, CH_3S), 3.70 (9H, m, 3xCH_3O), 3.82 (9H, m, 3xCH_3OOC), 4.14 (2H, s, CH_2Ar), 4.24 (4H, m, 2xCH_2Ar), 7.10 (3H, m, 3xAr-H), 7.24 (6H, m, 3x2Ar-H), 7.46 (3H, m, 3xAr-H) and 7.58 (3H, m, 3x=$CHCH_2$).

Compound 62

^{1}H N.M.R. δ(ppm) 1.08 (9H, s, $C(CH_3)_3$), 1.15 (9H, s, $C(CH_3)_3$), 2.38 (3H, s, CH_3S), 2.48 (3H, s, CH_3S), 3.66 (6H, s, 2xCH_3O), 3.82 (6H, m, 2xCH_3OOC), 4.14 (2H, s, CH_2Ar), 4.26 (2H, s, CH_2Ar), 7.10 (2H, m, 2xAr-H), 7.26 (4H, m, 2x2Ar-H), 7.44 (2H, m, 2xAr-H) and 7.56 (4H, m, 2x=$CHOCH_3$ and 2xN=$CHC(CH_3)_3$).

Compound 63

^{1}H N.M.R. δ(ppm) 1.00-1.18 (12H, m, 4x$\underline{CH_3}$CH), 1.90 (3H, s, $\underline{CH_3}$C=), 1.94 (3H, s, $\underline{CH_3}$S=), 1.98 (3H, s, $\underline{CH_3}$C=), 2.05 (3H, s, $\underline{CH_3}$C), 2.24-2.50 (8H, m, 4x$\underline{CH_2}$CH$_3$), 2.38 (6H, m, 2x$\underline{CH_3}$S), 2.46 (6H, m, 2x$\underline{CH_3}$S), 3.68 (12H, s, 4x$\underline{CH_3}$O), 3.82 (12H, m, 4x$\underline{CH_3}$OOC), 4.14 (4H, m, 2x$\underline{CH_2}$Ar), 4.26 (4H, m, 2x$\underline{CH_2}$Ar), 7.10 (4H, m, 4xAr-$\underline{H}$), 7.26 (8H, m, 4x2Ar-$\underline{H}$), 7.48 (4H, m, 4xAr-$\underline{H}$) and 7.60 (4H, m, 4x=$\underline{CH}$CH$_3$).

Compound 64

^{1}H N.M.R. δ(ppm) 1.84 (6H, m, 2x$\underline{CH_3}$C=), 1.92 (3H, s, $\underline{CH_3}$C=), 1.98 (3H, s, $\underline{CH_3}$C=), 2.40 (6H, m, 2x$\underline{CH_3}$S), 2.46 (6H, m, 2x$\underline{CH_3}$S), 3.59-3.88 (32H, 4x$\underline{CH_3}$O, 4x$\underline{CH_3}$OOC and 4x-C$\underline{CH_2}$), 4.18 (4H, s, 2x$\underline{CH_2}$Ar), 4.24 (2H, s, $\underline{CH_2}$Ar), 4.30 (2H, s, $\underline{CH_2}$Ar), 7.10 (8H, m, 4x2Ar-$\underline{H}$), 7.24 (24H, m, 4x6Ar-$\underline{H}$), 7.48 (4H, m, 4xAr-$\underline{H}$) and 7.56 (4H, m, 4x=$\underline{CH}$OCH$_3$).

Compound 65

^{1}H N.M.R. δ(ppm) 2.54 (6H, s, 2x$\underline{CH_3}$S), 3.66 (6H, m, 2x$\underline{CH_3}$OC), 3.82 (6H, m, 2x$\underline{CH_3}$OOC), 3.96 (6H, m, 2xC$\underline{H_3}$OPy), 4.18 (4H, s, 2x$\underline{CH_2}$Ar), 6.72 (2H, m, 2xPy-$\underline{H}$), 7.14 (2H, m, 2xAr-$\underline{H}$), 7.26 (4H, m, 2x2 Ar-$\underline{H}$), 7.48 (2H, m, 2xPy-$\underline{H}$), 7.60 (2H, m, 2x=$\underline{CH}$OCH$_3$), 8.08 (2H, m, 2xPy-$\underline{H}$) and 8.28 (4H, m, 2xPy-$\underline{H}$, 2xN=$\underline{CH}$Py).

Compound 66

^{1}H N.M.R. δ(ppm) 2.04 (3H, s, $\underline{CH_3}$C=), 2.10 (3H, s, $\underline{CH_3}$C=), 2.16 (3H, s, $\underline{CH_3}$C=), 2.18 (3H, s, $\underline{CH_3}$C=), 2.42 (3H, s, $\underline{CH_3}$S), 2.35 (3H, s, $\underline{CH_3}$S), 3.66 (3H, s, $\underline{CH_3}$O), 3.68 (3H, s, $\underline{CH_3}$O), 3.80 (6H, m, 2x$\underline{CH_3}$OOC), 3.96 (3H, s.$\underline{CH_3}$ON), 3.98 (3H, s, $\underline{CH_3}$ON), 4.16 (2H, s, $\underline{CH_2}$Ar), 4.35 (2H, s, $\underline{CH_2}$Ar), 7.12 (2H, m, 2xAr-$\underline{H}$), 7.26 (4H, m, 2x2Ar-$\underline{H}$), 7.46 (2H, m, 2xAr-$\underline{H}$) and 7.58 (2H, m, 2x=$\underline{CH}$OCH$_3$).

Compound 67

^{1}H N.M.R. δ(ppm) 2.44 (3H, s, CH_3S), 2.56 (3H, s, CH_3S), 3.64 (3H, s, CH_3O), 3.66 (3H, s, CH_3O), 3.80 (3H, s, CH_3OOC), 3.82 (3H, s, CH_3OOC), 4.22 (2H, s, CH_2Ar), 4.38 (2H, s, CH_2Ar), 7.12 (2H, m, 2xAr-H), 7.26 (4H, m, 2x2Ar-H), 7.38 (6H, m, 3x2Ar-H), 7.50 (2H, m, 2xAr-H), 7.60 (2H, m, 2x-$CHOCH_3$), 7.78 (4H, m, 2xAr-H), 8.32 (1H, s, N=CHAr) and 8.36 (1H, s, N=CHAr).

Compound 69

^{1}H N.M.R. δ(ppm) 2.44 (3H, s CH_3S), 2.52 (3H, s, CH_3S), 2.88 (6H, m, 2xCH_3NH), 3.96 (6H, m, 2xCH_3ON), 4.16 (2H, s, CH_2Ar), 4.28 (2H, s, CH_2Ar), 6.74 (2H, s, 2xNH), 7.06 (2H, m, 2xHet-H), 7.17 (2H, m, 2xAr-H), 7.40 (8H, m, 2x2Het-H and 2Ar-H), 7.50 (2H, m, 2xAr-H) and4 (2H, m, 2xN=CH-Het).

Compound 70

^{1}H N.M.R. δ(ppm) 2.46 (3H, s, CH_3S), 2.74 (3H, s, CH_3S), 2.88 (6H, m, 2xCH_3NH), 3.90 (3H, s, CH_3ON), 3.97 (3H, s, CH_3ON), 4.18 (2H, s, CH_2Ar), 4.55 (2H, s, CH_2Ar), 6.76 (2H, s, 2xNH), 7.06 (2H, m, 2xHet-H), 7.16 (2H, m, 2xAr-H), 7.34 (6H, m, 2x2xHet-H, 2x2Ar-H), 7.52 (4H, m, 2xHet-H and 2xAr-H), 7.98 (1H, s, N=CH-Het) and 8.04 (1H, s, N=CH-Het).

Compound 71

^{1}H N.M.R. δ(ppm) 2.42 (3H, s, CH_3S), 2.52 (3H, s, CH_3S), 3.80 (3H, s, CH_3ON), 3.82 (3H, s, CH_3ON), 4.08 (6H, s, 2xCH_3OOC), 4.15 (2H, s, CH_2Ar), 4.28 (2H, s, CH_2Ar), 7.05 (2H, m, 2xHet-H), 7.14 (2H, m, 2xAr-H), 7.32 (8H, m, 2x2Het-H), 7.54 (2H, m, 2xAr-H), 8.42 (1H, s, N=CH-Het) and 8.44 (N=CH-Het).

Compound 72

^{1}H N.M.R. δ(ppm) 2.46 (3H, s, CH_3S), 2.54 (3H, s, CH_3S), 3.83 (6H, s, CH_3ON), 4.02 (3H, s, CH_3OOC), 4.06 (3H, s, CH_3OOC), 4.17 (2H, s, CH_2Ar), 4.54 (2H, s, CH_2Ar), 7.06 (2H, m, 2xHet-H), 7.14 (2H, m, 2xAr-H), 7.36 (6H, m, 2xHet-H and 2x2Ar-H), 7.56 (4H, m, 2xHet-H and 2xAr-H), 8.00 (1H, s, N=CH-Het) and 8.04 (1H, s, N=CH-Het).

Compound 74

^{1}H N.M.R. δ(ppm) 2.44 (3H, s, CH_3S), 2.56 (3H, s, CH_3S), 3.82 (3H, s, CH_3ON), 3.86 (3H, s, CH_3ON), 4.06 (3H, s, CH_3OOC), 4.07 (3H, s, CH_3OOC), 4.16 (2H, s, CH_2Ar), 4.30 (2H, s, CH_2Ar), 7.14 (2H, m, 2xAr-H), 7.36 (4H, m, 2x2Ar-H), 7.52 (4H, m, 2x2Ar-H), 7.64 (2H, m, 2xAr-H), 7.94 (4H, m, 2x2Ar-H), 8.34 (1H, s, N=CH-Ar) and 8.36 (1H, s, N=CHAr).

Compound 75

^{1}H N.M.R. δ(ppm) 2.44 (3H, s, CH_3S), 2.56 (3H, s, CH_3S), 3.81 (3H, s, CH_3ON), 3.85 (3H, s, CH_3ON), 4.07 (3H, s, CH_3OOC), 4.09 (3H, s, CH_3OOC), 4.14 (2H, s, CH_2Ar), 4.28 (2H, s, CH_2Ar), 7.14 (2H, m, 2xAr-H), 7.36 (10H, m, 5x2Ar-H), 7.55 (2H, m, 2xAr-H), 7.75 (4H, 2x2Ar-H), 8.30 (1H, s, N=CHAr) and 8.32 (1H, s, N=CHAr).

Compound 77

^{1}H N.M.R. δ(ppm) 2.44 (3H, s, CH_3S), 2.56 (3H, s, CH_3S), 3.82 (3H, s, CH_3ON), 3.84 (3H, s, CH_3ON), 4.05 (6H, s, 2 x CH_3OOC), (4.15 (2H, s, CH_2Ar), 4.28 (2H, s, CH_2Ar), 7.14 (2H, m, 2xAr-H), 7.28-7-67 (10H, m, 2x5Ar-H), 7.84 (2H, m, 2Ar-H), 8.20 (2H, s, N=CHAr) and 8.22 (1H, s, N=CHAr).

Compound 83

^{1}H N.M.R. δ(ppm) 2.42 (3H, s, CH_3S), 2.55 (3H, s, CH_3S), 3.80 (3H, s, CH_3O), 3.84 (3H, s, CH_3O), 4.08 (3H, s, CH_3OOC), 4.10 (3H, s, CH_3OOC), 4.14 (2H, s, CH_2Ar), 4.30 (2H, s, CH_2Ar), 6.99-7.56 (26H, m, 2x13Ar-H), 8.26 (1H, s, ArCH=N) and 8.28 (1H, s, ArCH=N).

Compound 86

^{1}H N.M.R. δ(ppm) 2.48 (3H, s, CH_3S), 2.55 (3H, s, CH_3S), 3.84 (3H, s, CH_3O), 3.90 (3H, s, CH_3O), 4.08 (3H, s, CH_3OOC), 4.10 (3H, s, CH_3OOC), 4.18 (2H, s, CH_2Ar), 4.31 (2H, s, CH_2-Ar), 7.05-8.95 (16H, m, 2x8Ar-H), 8.35 (1H, s, ArCH=N) and 8.37 (1H, s, ArCH=N).

Compound 87

^{1}H N.M.R. δ(ppm) 2.48 (3H, s, CH_3S), 2.56 (3H, s, CH_3S), 2.56 (3H, s, CH_3S), 3.81 (3H, s, CH_3O), 3.84 (3H, s, CH_3O), 4.09 (6H, s, 2xCH_3OOC), 4.19 (2H, s, CH_2Ar), 4.30 (2H, s, CH_2Ar), 7.14-8.64 (16H, m, 2x8Ar-H), 8.25 (1H, s, Ar-CH=N) and 8.26 (1H, s, Ar-CH=N).

Compound 89

^{1}H N.M.R. δ(ppm) 2.46 (3H, s, CH_3S), 2.59 (3H, s, CH_3S), 2.94 (6H, m, 2x$NHCH_3$), 3.97 (3H, s, CH_3O), 3.99 (3H, s, CH_3O), 4.13 (2H, s, CH_2Ar), 4.32 (2H, s, CH_2Ar), 6.78 (2H, m, 2x13Ar-H) and 8.27 (1H, s, Ar-CH=N).

Compound 94

^{1}H N.M.R. δ(ppm) 2.46 (3H, s, CH_3S), 2.58 (3H, s, CH_3S), 2.4-2.94 (6H, m, 2x$NHCH_3$), 3.99 (6H, m, s, 2xCH_3O), 4.20 (2H, s, CH_2Ar), 4.33 (2H, s, CH_2Ar), 6.80 (2H, m, 2xCH_3NH), 7.14-8.64 (16H, m, 2x4Ar-H, 2x4Het-H), 8.37 (1H, s, Ar-CH=N) and 8.38 (1H, s, Ar-CH=N).

Compound 101

^{1}H N.M.R. δ(ppm) 1.24 (12H, m, $(CH_3)_2Cx2$), 2.44 (3H, s, CH_3S), 2.55 (3H, s, CH_3S), 2.94 (2H, m, $(CH_3)_2CHx2$), 3.81 (3H, s, CH_3O), 3.85 (3H, s, CH_3O), 4.06 (3H, s, CH_3O_2C), 4.10 (3H, s, CH_3O_2C), 4.17 (2H, s, CH_2Ar), 4.32 (2H, s, CH_2Ar), 7.15-7.77 (16H, m, 2x8Ar-H), 8.32 (1H, s, CH=N) and 8.35 (1H, s, CH=N).

Compound 104

^{1}H N.M.R. δ(ppm) 2.43 (3H, s, CH_3O), 2.57 (2H, s, CH_3S), 3.09 (6H, s, CH_3Sx2), 3.83 6H, s, $2xOCH_3$), 4.06 (6H, s, $2xCH_3O_2C$), 4.1 (6H, s, $2xCH_3O_2C$), 4.16 (4H, s, $2xCH_2Ar$), 4.30 (4H, s, $2xCH_2Ar$) and 7.0-7.9 (32H, m, 4x8Ar-H).

Compound 105

^{1}H N.M.R. δ(ppm) 2.30 (6H, s, Ar-CH_3x2), 2.42 (6H, s, Ar-CH_3x2), 2.56 (3H, s, CH_3O), 2.64 (3H, s, CH_3S), 3.82 (3H, s, CH_3O), 3.86 (3H, s, CH_3O_2C), 4.07 (3H, s, CH_3O_2C), 4.14 (2H, s, CH_2Ar), 4.30 (2H, s, CH_2Ar), 7.0-7.8 (14H, m, 2x7Ar-H), 8.30 (1H, s, CH=N) and 8.33 (1H, s, CH=N).

Compound 107

^{1}H N.M.R. δ(ppm) 2.35 (3H, s, CH_3Ar), 2.38 (3H, s, CH_3Ar), 2.42 (3H, s, CH_3Ar), 2.48 (3H, s, CH_3Ar), 2.58 (3H, s, CH_3S), 2.70 (3H, s, CH_3S), 3.82 (3H, s, CH_3O), 3.90 (3H, s, CH_3O), 4.08 (3H, s, CH_3O_2C), 4.10 (3H, s, CH_3O_2C), 4.18 (2H, s, CH_2Ar), 4.38 (2H, s, CH_2Ar), 7.1-7.78 (14H, m, 2x7Ar-H), 8.59 (1H, s, CH=N) and 8.60 (1H, s, CH=N).

Compound 108

^{1}H N.M.R. δ(ppm) 2.52 (3H, s, CH_3S), 2.62 (3H, s, CH_3S), 3.8 (3H, s, CH_3O), 3.88 (3H, s, CH_3O), 4.08 (3H, s, CH_3O_2C), 4.10 (3H, s, CH_3O_2C), 4.2 (2H, s, CH_2Ar), 4.4 (2H, s, CH_2Ar), 7.14-8.0 (22H, m, 2x11Ar-H), 8.98), (1H, s, CH=N) and 9.04 (1H, s, CH=N).

Compound 109

^{1}H N.M.R. δ(ppm) 1.14 (6H, m, CH_3CH_2x2), 2.48 (3H, s, CH_3S), 2.58 (3H, s, CH_3S), 2.90 (4H, m, CH_2CH_3x2), 3.80 (3H, s, CH_3O), 3.86 (3H, s, CH_3O), 4.08 (3H, s, CH_3O_2C), 4.09 (3H, s, CH_3O_2C), 4.16 (2H, s, CH_2Ar), 4.34 (2H, s, CH_2Ar) and 7.06-7.98 (18H, m, 2x9Ar-H).

Compound 110

^{1}H N.M.R. δ(ppm) 0.94 (6H, m, CH_3CH_2x2), 1.58 (4H, m, CH_2CH_3x2), 2.44 (3H, s, CH_3O), 2.59 (3H, s, CH_3S), 2.90 (4H, m, CH_2CH_2x2), 3.82 (3H, s, CH_3O), 3.88 (3H, s, CH_3O), 4.08 (3H, s, CH_3O_2C), 4.09 (3H, s, CH_3O_2C), 4.15 (2H, s, CH_2Ar), 4.34 (2H, s, CH_2Ar) and 7.04-7.94 (18H, m, 2x9Ar-H).

Compound 111

^{1}H N.M.R. δ(ppm) 1.96-2.0 (3H, s, CH_3Ox4), 2.40 (3H, s, CH_3S), 2.46 (3H, s, CH_3O), 2.47 (3H, s, CH_3O), 2.64 (8H, m, CH_2CH_2x4), 2.96 (8H, m, CH_2CH_2x4), 3.86 (12H, m, CH_3Ox4), 4.08 (12H, m, CH_3O_2Cx4), 4.12 (4H, br.s, CH_2Arx2), 4.20 (4H, br.s, CH_2Arx2) and 7.08-7.6 (36H, m, 4x9Ar-H).

Compound 153

^{1}H N.M.R. δ(ppm) 2.39 (3H, s, N=CCH_3), 2.41 (3H, s, N=CCH_3), 2.50 (3H, s, CH_3S), 2.59 (3H, s, CH_3S), 2.90-2.95 (6H, m, 2xNHCH_3), 3.02 (6H, m, 2xCH_3SO_2), 3.99 (6H, 2xs, 2xCH_3O), 4.20 (2H, s, CH_2Ar), 4.38 (2H, s, CH_2Ar), 6.80 (2H, m, 2xCH_3NH) and 7.14-8.10 (16H, m, 2x8Ar-H).

Compound 158

^{1}H N.M.R. δ(ppm) 2.50 (3H, s, CH_3S), 2.60 (3H, s, CH_3S), 3.10 (6H, 2xs, 2xCH_3SO_2), 3.86 (3H, s, CH_3O), 3.91 (3H, s, CH_3O), 4.07 (6H, 2xs, 2xCH_3OOC), 4.19 (2H, s, CH_2Ar), 4.34 (2H, s, CH_2Ar), 7.14-7.56 (8H, m, 2x4Ar-H), 7.95 (8H, m, 2x4Ar-H), 8.37 (1H, s, Ar-CH=N) and 8.39 (1H, s, Ar-CH=N).

Compound 168

^{1}H N.M.R. δ(ppm) 1.95-2.05 (4x3H, 4s, CH_3C), 2.41 (3H, s, CH_3S), 2.92 (2x3H, 2xd, CH_3N), 3.95 (3H, s, CH_3O), 3.99 (3H, s, CH_2Ar), 4.22 (2H, s, CH_2Ar), 6.76 (2H, s, 2xNH) and 7.12-7.54 (8H, m, 2x4Ar-H).

Compound 170

^{1}H N.M.R. δ(ppm) 1.15 (9H, s, $(CH_3)_3C$), 1,83 (3H, s, $CH_3C=N$), 1.92 (6H, s, $2xCH_3C=N$), 2.39 (3H, s, CH_3S), 2.50 (3H, s, CH_3S), 2.93 (3x3H, 2xd, CH_3N), 3.95 (3H, s, CH_3O), 3.95 (3H, s, CH_3O), 4.09 (2H, s, CH_2Ar), 4.22 (2H, s, CH_2Ar), 6.77 (2H, s, 2xNH) and 7.12-7.54 (8H, m, 2x4Ar-H).

Compound 175

^{1}H N.M.R. δ(ppm) 1.89-1.95 (4x3H, s, CH_3S), 2.41 (3H, s, CH_3S), 2.45 (3H, s, CH_3S), 2.90 (6H, d, $2xCH_3N$), 3.95 (2x3H, 2xs, CH_3O), 4.14 (2H, s, CH_2Ar), 4.27 (2H, s, CH_2Ar), 6, (1H, d, $=CHCH=$), 6.77 (2H, s, 2xNH), 7.13-7.53 (8H, m, 2x4Ar-H) and 8.14 (2H, m, 2xN=CH).

Compound 176

^{1}H N.M.R. δ(ppm) 2.35-2.50 (18H, m, SCH_3 and $=CCH_3$), 2.85-2.95 (9H, m, $CONHCH_3$), 3.90 (3H, s, $NCCH_3$), 3.95 (3H, s, $NCCH_3$), 4.00 (3H, s, $NCCH_3$), 4.15 (2H, s, CH_2Ar), 4.25 (2H, s, CH_2Ar), 4.50 (2H, s, CH_2Ar). 6.75 (3H, m, $3xCH_3NH$), 6.80-7.60 (18H, m, 3x4Ar-H and 3x2Het-H), 7.95 (1H, s, N=CH), 8.30 (1H, s, N=CH) and 8.35 (1H, s, N=CH).

Compound 177

^{1}H N.M.R. δ(ppm) 2.45 (3H, s, SCH_3), 2.50 (3H, s, SCH_3), 2.55 (3H, s, SCH_3), 2.65 (3H, s, SCH_3), 2.90-2.95 (12H, m, $CONHCH_3$), 3.95 (3H, s, $NCCH_3$), 4.00 (9H, m, $NCCH_3$), 4.15 (2H, s, Ar-CH_2), 4.20 (2H, s, Ar-CH_2), 4.35 (2H, s, Ar-CH_2), 4.50 (2H, s, Ar-CH_2), 6.95 (4H, m, $4xCH_3NH$), 7.20-7.60 (24H, m, 4xAr-H), 4x2Het-H), 7.95 (1H, s, N=CH), 8.00 (1H, s, N=CH) and 8.40 (2H, m, N=CH).

Compound 178

^{1}H N.M.R. δ(ppm) 2.45 (3H, s, SCH$_3$), 2.50 (3H, s, SCH$_3$), 2.55 (3H, s, SCH$_3$), 2.75 (3H, s, SCH$_3$), 3.90 (12H, m, CONHCH$_3$), 3.95 (6H, s, NOCH$_3$), 4.00 (6H, s, NOCH$_3$), 4.15-4.20 (4H, m, Ar-CH$_2$), 4.25 (2H, s, Ar-CH$_2$), 4.50 (2H, s, Ar-CH$_2$), 6.80-6.90 (4H, m, 4xCH$_3$NH), 7.04-7.55 (24H, m, 4x4Ar-H and 4x2Het-H) and 7.90 (2H, m, N=CH).

Compound 179

^{1}H N.M.R. δ(ppm) 2.40 (12H, s, N=CCH$_3$ and =CCH$_3$), 2.50 (3H, s, S-CH$_3$), 2.55 (3H, s, SCH$_3$), 3.90 (6H, m, CONHCH$_3$), 3.95 (6H, s, NOCH$_3$), 4.15 (2H, Ar-CH$_2$), 4.25 (2H, s, Ar-CH$_2$), 4.25 (2H, s, Ar-CH$_2$), 6.80 (2H, m, 2xCH$_3$NH) and 6.90-7.55 (12H, m, 2x4Ar-H and 2x2Het-H).

Compound 180

^{1}H N.M.R. δ(ppm) 2.25-2.50 (21H, m, N=CCH$_3$ and SCH$_3$), 2.75 (3H, s, S-CH$_3$), (12H, m, CONHCH$_3$), 3.95-4.05 (12H, m, NOCH$_3$), 4.15 (4H, m, Ar-CH$_2$), 4.25 (2H, m, Ar-CH$_2$), 4.50 (2H, s, Ar-CH$_2$), 6.78 (4H, m, 4xCH$_3$NH), 6.90 (4H, m, 4xHet-H), 7.14-7.60 (20H, m, 4x4Ar-H and 4xHet-H).

Compound 184

^{1}H N.M.R. δ(ppm) 2.40 (3H, s, SCH$_3$), 2.55 (3H, s, SCH$_3$), 2.95 (6H, m, CONHCH$_3$), 4.00 (6H, s, NOCH$_3$), 4.20 (2H, s, Ar-CH$_2$), 4.30 (2H, s, Ar-CH$_2$), 6.85 (2H, m, 2xCH$_3$NH), 7.15-7.66 (14H, m, 2x4Ar-H and 2x3Het-H) and 8.35 (2H, m, N=CH).

Compound 186

^{1}H N.M.R. δ(ppm) 2.42 (3H, s, CH$_3$S), 2.43 (3H, s, CH$_3$S), 2.44 (3H, s CH$_3$S), 2.82-3.00 (12H, m, 3xSCH$_2$CH$_2$), 2.96 (9H, m, 3xNHCH$_3$), 3.61 (6H, m, 3xNCCH$_2$S), 3.98 (9H, m, 3xCH$_3$ON), 4.16 (2H, s, CH$_2$Ar), 4.23 (4H, m, 2xCH$_2$Ar), 6.80 (3H, m, 3xNHCH$_3$) and 7.10-7.56 (12H, m, 3x4Ar-H).

Compound 187

^{1}H N.M.R. δ(ppm) 2.42 (3H, s, CH_3S), 2.44 (3H, s, CH_3S), 2.61-2.79 (8H, m, 2xCH_2SCH_2), 2.81-2.90 (8H, m, 2x=$CH_2)_2$), 2.93 (6H, m, 2xCH_3NH), 3.97 (3H, s, CH_3ON), 3.99 (3H, s, CH_3ON), 3.99 (3H, s, CH_3ON), 4.10 (2H, s, CH_2Ar), 4.20 (2H, s, CH_2Ar), 6.80 (2H, m, 2xCH_3NH), 7.13-7.55 (8H, m, 2x4ArH).

Compound 188

^{1}H N.M.R. δ(ppm) 2.35-2.62 (18H, m, 3xCH_3S and 3xCH_3C=), 2.96 (9H, m, 3xCH_3NH), 3.94 (3H, s, CH_3ON), 3.96 (3H, s, CH_3ON), 3.97 (3H, s, CH_3ON), 4.18 (2H, s, CH_2Ar), 4.30 (2H, s, CH_2Ar), 4.40 (2H, s, CH_2Ar), 6.10 (3H, m, 3x=CH), 6.72 (3H, m, 3x=CH), 6.82 (3H, m, 3xCH_3NH), 7.17-7.58 (12H, m, 3x4Ar-H) and 8.10 (3H, m, 3xN=CH).

Compound 190

^{1}H N.M.R. δ(ppm) 1.14(9H, m, 3xCH_3CH_2), 2.42 (3H, s, CH_3S), 2.43 (3H, s, CH_3S), 2.50 (3H, s, CH_3S), 2.72 (6H, m, 3xCH_2CH_3), 2.90 (9H, m, 3xCH_3NH), 3.90 (3H, s, CH_3S), 3.85 (3H, s, CH_3ON), 3.87 (3H, s, CH_3ON), 4.15 (2H, CH_2Ar), 4.28 (2H, s, CH_2Ar), 4.38 (2H, s, CH_2Ar), 6.10 (3H, m, 3x=CH), 6.74 (3H, m, 3x=CH), 6.80 (3H, m, CH_3NH), 7.18-7.58 (12H, m, 3x4Ar-H) and 8.08 (3H, m, 3xN=CH).

Compound 191

^{1}H N.M.R. δ(ppm) 1.95 (9H, m, 3xCH_3C=), 2.24 (9H, m, CH_3C=), 2.40 (3H, s, CH_3S), 2.41 (3H, s, CH_3S), 2.48 (3H, m, CH_3S), 2.94 (9H, m, 3xCH_3NH), 3.95 (9H, m, 3xCH_3ON), 4.16 (2H, s, CH_2Ar), 4.26 (4H, m, 2xCH_2Ar), 6.60 (3H, m, 3x=CH), 6.75 (3H, m , 3xCH_3NH), 7.08-7.55 (12H, m, 3x4Ar-H) and 8.02 (3H, m, 3xN=CH).

Compound 192

^{1}H N.M.R. δ(ppm) 2.42 (3H, s, CH_3S), 2.44 (3H, s, CH_3S), 2.50 (3H, s, CH_3S), 2.90 (9H, m, 3xCH_3NH), 3.95 (9H, m, 3xCH_3ON), 4.17 (2H, s, CH_2Ar), 4.28 (2H, s, CH_2Ar), 4.35 (2H, s, CH_2Ar), 6.40 (3H, m, 3x=CH), 6.74 (3H, m, 3x=CH), 6.80 (3H, m, 3xCH_3NH), 7.10-7.55 (12H, m, 3x4Ar-H) and 8.06 (3H, m, 3xN=CH).

Compound 193

^{1}H N.M.R. δ(ppm) 1.10-1.42 (24H, m, 4x$CH_2CH_2CH_2$), 1.60-1.90 (16H, m, 4xCH$(CH_2)_2$), 2.28-2.50 (16H, m, 4x=CH_3S), 2.92 (12H, m, 4xCH_3NH), 3.98 (12H, m, 4xCH_3ON), 4.15 (2H, s, CH_2Ar), 4.23 (4H, m, 2xCH_2Ar), 4.40 (2H, m, CH_2Ar), 6.97 (4H, m, 4xCH_3NH), 7.10-7.55 (16H, m, 4x4Ar-H) and 7.62 (4H, m, 4xN=CH).

Compound 194

^{1}H N.M.R. δ(ppm) 1.10-2.75 (28H, m, 4x3CH_2 and 4xCH$(CH_2)_2$), 2.40-2.52 (12H, m, 4xCH_3S), 2.94 (12H, m, 4xCH_3NH), 3.98 (12H, m, 4xCH_3ON), 4.15 (2H, s, CH_2Ar), 4.22 (6H, m, 3xCH_2Ar), 5.70 (8H, m, 4xCH=CH), 6.78 (4H, m, 4xCH_3NH), 7.14-7.58 (16H, m, 4x4Ar-H) and 7.68 (4H, m, 4xCH=N).

Compound 196

^{1}H N.M.R. δ(ppm) 2.47 (3H, s, CH_3S), 2.57 (3H, s, CH_3S), 3.04 (6H, s, $(CH_3)_2N$), 3.07 (6H, s, $(CH_3)_2N$), 3.86 (3H, s, CH_3ON), 3.89 (3H, s, CH_3ON), 4.10 (2x3H, 2xs, CH_3O_2C), 4.15? (2H, s, CH_2Ar), 4.32 (2H, s, CH_2Ar), 6.73 (2H, d, 2xAr-H), 7.15-7.65 (6H, 2x3Ar-H), 8.25 (1H, s, CH=N) and 8.27 (1H, s, CH=N).

Compound 197

^{1}H N.M.R. δ(ppm) 2.47 (3H, s, CH_3S), 2.61 (3H, s, CH_3S), 2.70 (3H, s, CH_3S), 3.85 (3H, s, CH_3ON), 3.91 (6H, s, 2xCH_3ON), 4.10 (3H, s, CH_3OOC), 4.13 (6H, s, 2 x CH_3OOC), 4.19 (2H, s, CH_2Ar), 4.36 (4H, m, 2xCH_2Ar), 7.17-7.75 (21H, m, 3x7Ar-H), 8.22 (5H, m, 3xAr-H and 2xN=CH) and 8.73 (1H, s, N=CH).

Compound 198

^{1}H N.M.R. δ(ppm) 1.97 (3H, s, $CH_3C=N$), 1.99 (3H, s, $CH_3C=N$), 2.07 (3H, s, $CH_3C=N$), 2.04 (3H, s, $CH_3C=N$), 2.42 (3H, s, CH_3C), 2.5 (3H, s, CH_3S), 3.89 (6H, s, 2xCH_3ON), 4.06 (3H, s, CH_3O_2C), 4.08 (3H, s, CH_3O_2C), 4.13 (2H, s, CH_2Ar), 4.23 (2H, s, CH_2Ar) and 7.13-7.59 (8H, m, 2x4ArH).

Compound 199

^{1}H N.M.R. δ(ppm) 2.39 (3H, s, $CH_3C=N$), 2.42 (3H, s, $CH_3C=N$), 2.46 (3H, s, CH_3S), 2.59 (3H, s, CH_3S), 3.83 (3H, s, CH_3ON), 3.90 (3H, s, CH_3ON), 4.09 (3H, s, CH_3SO_2C), 4.11 (3H, s, CH_3O_2C), 4.18 (2H, s, CH_2Ar), 4.36 (2H, s, CH_2Ar) and 7.16-7.93 (18H, m, 2x9ArH).

Compound 200

^{1}H N.M.R. δ(ppm) 1.16 (9H, s, $(CH_3)_3C$), 1.2 (9H, s, $(CH_3)_3C$), 1.88 (3H, s, $CH_3C=N$), 1.93 (3H, s, $CH_3OC=N$), 2.42 (3H, s, CH_3S), 2.52 (3H, s, CH_3S), 3.87 (3H, s, CH_3ON), 3.88 (3H, s, CH_3ON), 4.08 (3H, s, CH_3S), 4.09 (3H, s, CH_3O_2C), 4.13 (2H, s, CH_2Ar), 4.23 (2H, s, CH_2Ar) and 7.14-7.58 (8H, m, 2x4ArH).

Compound 201

^{1}H N.M.R. δ(ppm) 2.48 (12H, m, 4x=CCH_3), 2.60-2.70 (12H, m, 4xCH_3S), 3.83 (3H, s, CH_3ON), 3.90 (9H, m, 4xCH_3ON), 4.04-4.16 (18H, 4xCH_3OOC and 3xCH_2Ar), 4.35 (2H, s, CH_2Ar), 7.18-7.76 (24H, m, 4x4Ar-H), 8.23 (4H, m, 4xHet-H) and 8.62 (4H, m, 4xHet-H).

Compound 202

^{1}H N.M.R. δ(ppm) 2.32 (3H, s, =C$\underline{CH_3}$), 2.36 (3H, s, =C$\underline{CH_3}$), 2.40 (3H, s, =CCH_3), 2.48 (6H, m, $\underline{CH_3}$S and =C$\underline{CH_3}$), 2.60 (6H, m, 2x$\underline{CH_3}$S), 2.72 (3H, s, $\underline{CH_3}$S), 3.82 (3H, s, $\underline{CH_3}$ON), 3.90 (9H, m, 3x$\underline{CH_3}$ON), 4.10 (12H, m, 4x$\underline{CH_3}$OOC), 4.18 (4H, m, 2x$\underline{CH_2}$Ar), 4.35 (4H, s, 2x$\underline{CH_2}$Ar), 7.18-7.76 (24H, m, 4x4Ar-$\underline{H}$ and 4x2Het-$\underline{H}$) and 8.66 (8H, m, 4x2Het-$\underline{H}$).

Compound 203

^{1}H N.M.R. δ(ppm) 2.49 (3H, s, $\underline{CH_3}$S), 2.59 (3H, s, $\underline{CH_3}$S), 3.86 (3H, s, $\underline{CH_3}$ON), 3.91 (3H, s, $\underline{CH_3}$ON), 4.09 (3H, s, $\underline{CH_3}O_2C$), 4.10 (3H, s, $\underline{CH_3}O_2C$), 4.34 (2H, s, $\underline{CH_2}$Ar), 4.37 (2H, s, $\underline{CH_2}$Ar), 7.14-7.95 (12H, m, 2x6Ar$\underline{H}$), 8.49 (1H, s, $\underline{CH}$C=N) and 8.54 (1H, s, $\underline{CH}$C=N).

Compound 204

^{1}H N.M.R. δ(ppm) 2.50 (3H, s, $\underline{CH_3}$S), 2.61 (3H, s, $\underline{CH_3}$S), 3.86 (3H, s, $\underline{CH_3}$ON), 3.90 (3h, s, $\underline{CH_3}$ON), 4.10 (3H, s, $\underline{CH_3}O_2C$), 4.22 (2H, s, $\underline{CH_2}$Ar), 4.34 (2M, s, $\underline{CH_2}$Ar), 8.46 (18H, m, 2 x 9, Ar-$\underline{H}$), 8.53 (1H, s, $\underline{CH}$C=N), 8.56 (1H, s, $\underline{CH}$C=N), 9.35 (1H, d, Ar-$\underline{H}$) and 9.41 (1H, d, Ar$\underline{H}$).

Compound 207

^{1}H N.M.R. δ(ppm) 1.94 (3H, s, $\underline{CH_3}$C), 1.95 (3H, s, $\underline{CH_3}$C=C), 1.97 (3H, s, $\underline{CH_3}$C=C), 2.42 (3H, s, $\underline{CH_3}$S), 3.51 (3H, s, $\underline{CH_3}$S), 3.89 (3H, s, $\underline{CH_3}$ON), 3.40 (3H, s, $\underline{CH_3}$ON), 4.08 (6H, s, 2x$\underline{CH_3}O_2C$), 4.14 (2H, s, $\underline{CH_2}$Ar), 4.26 (2H, s, $\underline{CH_2}$Ar), 6.14 (1H, d, C=$\underline{CH}$C=), 7.13-7.57 (8H, m, 2x4 Ar-$\underline{H}$), 8.08-8.12 (1H, d, $\underline{CH}$C=N) and 8.10-8.15 (1H, d, $\underline{CH}$C=N).

Compound 213

^{1}H N.M.R. δ(ppm) 1.48 (6H, m, 2xCH_3C), 2.20 (3H, s, CH_3S), 2.23 (3H, s, CH_3S), 2.84 (3H, m, CH_3NH), 2.86 (3H, m, CH_3NH), 3.78 (2H, m, 2x=CHCHMe), 3.94 (3H, s, CH_3ON), 3.98 (3H, s, CH_3ON), 4.13 (2H, s, CH_2Ar), 4.19 (2H, s, CH_2Ar), 6.73 (2H, s, 2xNHMe), 7.10-7.55 (18H, m, 2x9ArH) and 7.62 (2H, m, 2x=CHCHMe).

Compound 214

^{1}H N.M.R. δ(ppm) 1.34 (6H, m, 2xCH_3CHCF_3), 2.40 (3H, s, CH_3S), 2.46 (3H, s, CH_3S), 2.90 (6H, m, 2xCH_3NH), 3.24 (2H, m, 2xCH_3CHCF_3), 3.94 (6H, s, 2xCH_3ON), 4.12 (2H, s, CH_2Ar), 4.22 (2H, s, CH_2Ar), 6.75 (2H, s, 2xNHMe), 7.14 (2H, m, 2xAr-H), 7.30 (4H, m, 2x2 Ar-H), 7.44 (2H , m, 2xAr-H) and 7.64 (2H, m, 2xN=CHCH).

Compound 215

^{1}H N.M.R. δ(ppm) 2.43 (6H, m, 2xCH_3S), 2.52 (3H, s, CH_3S), 2.70 (9H, m, 3xCH_3NH), 3.81 (9H, m, 3xCH_3OAr), 3.96 (9H, s, 3xCH_3ON), 4.16 (2H, s, CH_2Ar), 4.28 (4H, m, 2xCH_2Ar), 6.76 (3H, m, 3xCH_3NH), 6.82-6.95 (12H, m, 3x2ArH and 3xCH=CH), 7.14 (3H, m, 3xArH), 7.23-7.54 (15H, m, 3x5ArH) and 8.10 (3H, m, N=CH).

Compound 216

^{1}H N.M.R. δ(ppm) 2.40 (3H, s, CH_3S), 2.44 (3H, s, CH_3S), 2.40-2.75 (8H, m, 2x2CH_2CH_2C), 2.98 (6H, m, 2xCH_3NH), 3.66-3.86 (8H, m, 2x2CH_2CH_2C), 3.90 (3H, s, CH_3ON), 3.92 (3H, s, CH_3ON), 4.10 (2H, s, CH_2Ar), 4.19 (2H, s, CH_2Ar), 6.76 (2H, m, 2xCH_3NH), 7.14 (2H, m, 2xAr-H), 7.30 (4H, m, 2x2ArH) and 7.48 (2H, m, 2xArH).

Compound 217

^{1}H N.M.R. δ(ppm) 0.92 (18H, m, 3xCH(CH_2CH_3)$_2$), 1.50 (12H, m, 3xCH(CH_2CH_3)$_2$), 2.18 (3H, m, 3xCH(CH_2CH_3)$_2$), 2,38 (6H, m, 2xCH_3S), 2.44 (3H, s, CH_3S), 2.90 (9H, m, 3xCH_3NH), 3.94 (9H, s, 3xCH_3ON), 4.10 (2H, s, CH_2Ar), 4.22 (4H, m, 2xCH_2Ar), 6.76 (3H, m, CH_3NH), 7.14 (3H, m, 3xArH), 7.30 (6H, m, 2x2ArH) and 7.45 (6H, m, 3xNCH and 3xArH).

Compound 218

^{1}H N.M.R. δ(ppm) 1.07-2.10 (20H, m, 4x3CH and 4xCH_2), 2.20-2.25 (12H, m, 4xCH_3S), 2.92 (12H, m, 4xCH_3NH), 3.04 (8H, m, 4xCH_2 bridging), 3.96 (12H, m, 4xCH_3ON), 4.14 (2H, s, CH_2Ar), 4.22 (6H, m, 3xCH_2Ar), 6.00-6.23 (8H, m, 4xCH = CH), 6.75 (4H, m, 4 x CH_3NH), 7.15 (4H, m, 3 x Ar-H), 7.34 (8H, m, 4 x2ArH), 7.48 (4H, m, 4xArH) and 7.72 (4H, m, 4xN=CH).

Compound 219

^{1}H N.M.R. δ(ppm) 1.08 (3H, s, CH_3C), 1.15 (3H, s, CH_3C), 2.02 (4H, m, 2xCH_2CH), 2.38 (3H, s, CH_3S), 2.46 (3H, s, CH_3S), 2.95 (6H, m, 2xCH_3NH), 3.95 (6H, m, 2xCH_3ON), 4.12 (2H, s, CH_2Ar), 4.22 (2H, s, CH_2Ar), 5.02 (4H, m, 2xHC=CH_2), 5.80 (2H, m, 2xCH=CH_2), 6.75 (2H, s, 2xCH_3NH), 7.14 (2H, m, 2xArH), 7.30 (4H, m, 2x2ArH), 7.48 (2H, m, 2xArH), 7.55 (1H, s, N=CH) and 7.57 (1H, s, N=CH).

Compound 220

^{1}H N.M.R. δ(ppm) 1.08 (12H, m, 4xCH_3), 1.54-2.00 (8H, m, 4xCH_2), 2.35 (4H, m, 4xCHMe), 2.42 (6H, m, 2xCH_3S), 2.48 (6H, m, 2xCH_3S), 2.82 (4H, m, 4xCHMe), 2.88 (12H, m, 4xCH_3ON), 4.14 (4H, m, 2xCH_2Ar), 4.22 (4H, m, 2xCH_2Ar), 6.76 (4H, m, 4xCH_3NH), 7.08-7.42 (32H, m, 4x8ArH) and 7.52 (8H, m, 4xN=CH and 4xArH).

Compound 221

^{1}H N.M.R. δ(ppm) 2.35-2.70 (36H, m, =CCH_3, N=CCH_3 and S CH_3), 3.85 (3H, s, CH_3ON), 3.90 (9H, m, CH_3ON), 4.10 (12H, m, COOCH_3), 4.15-4.20 (4H, m, ArCH_2), 4.35 (4H, m, ArCH_2), 6.75 (4H, m, Het-H), 7.10-7.60 (20H, m, Ar-H), 7.90 (1H, s, N=CH), 7.95 (1H, s, N=CH) and 8.40 (2H, m, N=CH).

Compound 222

^{1}H N.M.R. δ(ppm) 2.40-2.50 (18H, m, =CCH_3 and SCH_3), 2.65 (3H, s, SCH_3), 2.75 (3H, s, SCH_3), 3.90 (12H, m, CH_3ON), 4.10 (12H, m, COOCH_3), 4.15 (4H, m, ArCH_2), 4.30 (2H, s, ArCH_2), 4.60 (2H, s, ArCH_2), 6.75 (4H, m, Het-H), 7.10-7.60 (20H, m, Ar-H), 7.90 (1H, s, N=CH), 7.95 (1H, s, N=CH) and 8.40 (2H, m, N=CH).

Compound 223

^{1}H N.M.R. δ(ppm) 2.45 (3H, s, SCH_3), 2.55 (3H, s, SCH_3), 3.85 (3H, s, CH_3ON), 3.90 (3H, s, CH_3ON), 4.10 (6H, m, COOCH_3), 4.15 (2H, m, ArCH_2), 4.30 (2H, s, ArCH_2), 7.15 (2H, m, ArH), 7.30-7.45 (6H, m, ArH), 7.50-7.70 (6H, m, ArH) and 8.35 (2H, m, N=CH).

Compound 224

^{1}H N.M.R. δ(ppm) 2.40 (3H, s, SCH_3), 2.50 (3H, s, SCH_3), 2.55 (3H, s, SCH_3), 2.75 (3H, s, SCH_3), 3.90 (12H, m, CH_3ON), 4.05-4.20 (12H, m, COOCH_3), 4.30 (4H, s, ArCH_2), 4.35 (2H, s, ArCH_2), 4.50 (2H, s, ArCH_2), 7.10-7.60 (30H, m, Ar-H), 7.95 (1H, s, N=CH), 8.00 (1H, s, N=CH) and 8.35 (2H, m, N=CH).

Compound 225

^{1}H N.M.R. δ(ppm) 2.45 (3, s, CH_3S), 2.50 (3H, s, CH_3S), 2.55 (3H, s, CH_3S), 2.75 (3H, s, CH_3S), 3.90 (12H, m, 4xCH_3ON), 4.12 (12H, m, 4xCH_3OOC), 4.15 (2H, s, CH_2Ar), 4.26 (2H, s, CH_2Ar), 4.38 (2H, s, CH_2Ar), 4.50 (2H, s, CH_2Ar), 7.00-7.60 (24H, m, 4x4Ar-H and 4x2Het-H), 7.85 (1H, s, NCH), 7.90 (1H, s, N=CH) and 8.30 (2H, m, 2xN=CH).

Compound 226

^{1}H N.M.R. δ(ppm) 1.35 (27H, m, $C(CH_3)_3$), 2.45 (3H, s, SCH_3), 2.55 (3H, s, SCH_2), 2.70 (3H, s, SCH_3), 3.85-3.90 (9H, m, CH_3ON), 4.10 (9H, CH_3OOC), 4.20 (2H, s, $ArCH_2$), 4.30 (2H, s, $ArCH_2$), 4.35 (2H, s, $ArCH_2$), 7.15-7.20 (3H, m, ArH), 7.30-7.50 (12H, m, ArH), 7.55-7.60 (3H, m, ArH), 7.65-7.80 (6H, m ArH), 7.85 (1H, s, N=CH) and 8.35 (2H, m, N=CH).

Compound 227

^{1}H N.M.R. δ(ppm) 2.30 (3H, s, $N=CCH_3$), 2.35 (3H, s, $N=CCH_3$), 2.45 (9H, m, $N=CCH_3SCH_3$), 2.50 (3H, s, SCH_3), 2.55 (3H, s, SCH_3), 2.75 (3H, s, SCH_3), 3.95 (12H, m, CH_3ON), 4.05 (12H, m, CH_3OOC), 4.10 (4H, m, $ArCH_2$), 4.30 (2H, s, $ArCH_2$), 4.50 (2H, s, $ArCH_2$), 6.85 (2H, m, Het-H), 7.10-7.20 (8H, m, ArH), 7.30-7.45 (8H, m, ArH) and 7.55-7.60 (4H, m, Ar-H).

Compound 228

^{1}H N.M.R. δ(ppm) 2.04 (12H, m, 4xCH_3S), 2.78-3.00 (16H, m, 4xCH_2CH_2S), 2.92 (12H, m, 4xCH_3NH), 3.58-3.68 (8H, m, 4x$N=CCH_2S$), 3.86 (12H, m, 4xCH_3ON), 4.06 (12H, m, 4xCH_3OOC), 4.10-4.21 (8H, m, 4xCH_2Ar) and 7.14-7.58 (16H, m, 4x4Ar-H).

Compound 229

^{1}H N.M.R. δ(ppm) 2.42 (3H, s, CH_3S), 2.44 (3H, s, CH_3S), 2.72 (8H, m, 2xCH_2SCH_2), 2.86 (8H, m, 2x=C(CH_2)$_2$), 3.84 (6H, s, 2xCH_3ON), 4.04-4.10 (10H, m, 2xCH_3OOC and 2xCH_2Ar) and 7.14-7.58 (8H, m, 2x4Ar-H).

Compound 230

^{1}H N.M.R. δ(ppm) 2.44 (3H, s, CH_3S), 2.52 (3H, s, CH_3S), 3.84 (3H, s, CH_3ON), 3.86 (3H, s, CH_3ON), 4.06 (6H, m, 2xCH_3OOC), 4.25 (2H, s, CH_2Ar), 4.34 (2H, s, CH_2Ar), 6.80-7.78 (14H, m, 2x4ArH and 2x3Het-H), 8.26 (1H, s, N=CH) and 8.30 (1H, s, N=CH).

Compound 231

^{1}H N.M.R. δ(ppm) 2.35-2.55 (12H, m, 2xCH_3S and 2xCH_3C=), 3.84 (6H, m, 2xCH_3ON), 4.06 (6H, s, CH_3OOC), 4.15 (2H, s, CH_2Ar), 4.30 (2H, s, CH_2Ar), 6.10 (2H, m, 2x=CH), 6.74 (2H, m, 2x=CH), 7.12-7.60 (8H, m, 2xArH), 8.10 (1H, s, N=CH) and 8.14 (1H, s, N=CH).

Compound 232

^{1}H N.M.R. δ(ppm) 2.46 (3H, s, CH_3S), 2.55 (3H, s, CH_3S), 3.84 (3H, s, CH_3ON), 3.86 (3H, s, CH_3ON), 4.08 (6H, s, 2xCH_3OOC), 4.21 (2H, s, CH_2Ar), 4.32 (2H, s, CH_2Ar) and 7.14-7.66 (18H, m, 2x8ArH and 2xHet-H).

Compound 233

^{1}H N.M.R. δ(ppm) 1.25 (9H, m, 3xCH_3CH_2), 2.48 (3H, s, CH_3S), 2.50 (3H, s, CH_3S), 2.54 (3H, s, CH_3S), 2.68-2.78 (6H, m, 3xCH_2CH_3), 3.86 (9H, m, 3xCH_3ON), 4.06 (9H, m, 3xCH_3OOC), 4.15 (2H, s, CH_2Ar), 4.28 (2H, s, CH_2Ar), 4.35 (2H, s, CH_2Ar), 6.10 (3H, m, 3x=CH), 6.74 (3H, m, 3x=CH), 7.15-7.60 (12H, m, 3x4Ar-H) and 8.14 (3H, m, 3xN=CH).

Compound 234

^{1}H N.M.R. δ(ppm) 2.42-2.66 (18H, m, 2xCH_3-C= and 2xCH_3S), 3.83 (3H, s, CH_3ON), 3.88 (3H, s, CH_3ON), 4.06 (6H, m, 2xCH_3OOC), 4.15 (2H, s, CH_2Ar), 4.30 (2H, s, CH_2Ar), 7.16-7.60 (8H, m, 2x4Ar-H) and 8.08 (2H, m, 2xN=CH).

Compound 235

^{1}H N.M.R. δ(ppm) 2.08-2.66 (36H, m, 4x3CH_3C= and 4xCH_3S), 3.86 (12H, m, 4xCH_3ON), 4.03 (3H, s, CH_3OOC), 4.08-44.18 (11H, m, 3xCH_3OOC and 1xCH_2Ar), 4.28 (2H, s, CH_2Ar), 4.35 (4H, m, 2xCH_2Ar), 6.63 (4H, m, 4xHC=), 7.1-7.62 (16H, m, 4x4Ar-H) and 8.00 (4H, s, 4xN=CH).

Compound 236

^{1}H N.M.R. δ(ppm) 2.24-2.68 (12H, m, 4xCH_3S), 3.86 (12H, m, 4xCH_3ON), 4.04-4.18 (14H, m, 4xCH_3OOC and1xCH_2Ar), 4.34 (6H, m, 3xCH_2Ar), 6.38-6.55 (4H, m, 4x=CH), 6.75-6.86 (4H, m, 4x=CH), 7.14-7.58 (16H, m, 4x4ArH) and 8.18 (4H, m, 4xN=CH).

Compound 237

^{1}H N.M.R. δ(ppm) 1.08-1.40 (24H, m, 4x$CH_2CH_2CH_2$), 1.62-1.94 (16H, m, 4xCH(CH_2)$_2$), 2.28-2.54 (16H, m, 4x=CH and 4xCH_3S), 3.88 (12H, m, 4xCH_3ON), 4.10-4.18 (14H, m, 4xCH_3OOC and 1xCH_2Ar), 4.24 (2H, s, CH_2Ar), 4.36 (2H, s, CH_2Ar), 4.38 (2H, s, CH_2Ar), 7.10-7.56 (16H, m, 4x4ArH) and 7.62 (4H, m, 4xN=CH).

Compound 238

^{1}H N.M.R. δ(ppm) 1.44-2.70 (28H, m, 4x3$CH_2$and 4x$CH(CH_2)_2$), 2.42-2.55 (12H, m, 4xCH_3S), 3.90 (12H, m, 4xCH_3ON), 4.04-4.17 (14H, m, 4xCH_3OOC and 1xCH_2Ar), 4.24 (4H, m, 2xCH_2Ar), 4.35 (2H, s, CH_2Ar), 5.70 (8H, m, 4xHC=CH), 7.14-7.58 (16H, m ,4x4ArH) and 7.72 (4H, m, 4xN=CH).

Compound 239

^{1}H N.M.R. δ(ppm) 1.14 (12H, m CH_3CHCH_3x2), 2.40 (3H, s, CH_3S), 2.48 (3H, s, CH_3S), 2.60 (2H, CH_3CHCH_3x2), 2.94 (6H, m, CH_3NHx2), 3.98 (6H, m, CH_3Ox2), 4.18 (2H, s, CH_2Ar), 4.21 (2H, s, CH_2Ar), 6.80 (2H, br.t, NHCH_3x2), 7.1-7.9 (10H, m, 2x4ArH and CH=Nx2).

Compound 242

^{1}H N.M.R. δ(ppm) 0.90 (6H, m, CH_3CH_2x2), 1.34 (8H, m, $CH_3CH_2CH_2$x2), 1.48 (8H, m, $CH_2CH_2CH_2CH_2$x2), 1.80 (4H, m, OCH_2CH_2x2), 2.46 (3H, s, CH_3S), 2.55 (3H, s, CH_3S), 2.90 (6H, m, CH_3NHx2), 3.98 (6H, m, CH_3Ox2), 4.17 (2H, s, CH_2Ar), 4.30 (2H, s, CH_2Ar), 6.80 (2H, br.t, NH CH_3 x2), 6.90-7.60 (16H, m, 2x8 ArH), 8.30 (2H, s, CH=N) and 8.33 (1H, s, CH=N).

Compound 243

^{1}H N.M.R. δ(ppm) 2.44 (3H, s, CH_3S), 2.58 (3H, s, CH_3S), 2.98 (6H, m, CH_3NHx2), 3.99 (6H, m, CH_3Ox2), 4.18 (2H, s, CH_2Ar), 4.26 (2H, s, CH_2Ar), 5.7-6.18 (2H, t, CHF_2x2), 6.79 (2H, br.s, NHCH_3x2), 7.38-7.78 (16H, m, 2x8ArH), 8.30 (1H, s, CH=N) and 8.32 (1H, s, CH=N).

Compound 244

^{1}H N.M.R. δ(ppm) 2.46 (3H, s, CH_3S), 2.60 (3H, s, CH_3S), 2.88 (3H, d, CH_3NH), 2.90 (3H, d, CH_3NH), 3.98 (3H, s, CH_3O), 4.00 (3H, s, CH_3O), 4.22 (2H, s, CH_2Ar), 4.38 (2H, s, CH_2Ar), 6.82 (2H, br.d, NHCH_3x2), 7.00-8.3 (22H, m, 2x11ArH), 8.35 (1H, s, CH=N) and 8.40 (1H, s, CH=N).

Compound 245

^{1}H N.M.R. δ(ppm) 2.42 (3H, s, CH_3S), 2.56 (3H, s, CH_3S), 2.94 (6H, d, CH_3NHx2), 3.98 (6H, s, CH_3Ox2), 4.18 (2H, s, CH_2Ar), 4.3 (2H, s, CH_2Ar), 6.8 (2H, br.m, $NHCH_3$x2), 6.94-7.18 (4H, m, CH=CHx2), 7.20-7.60 (18H, m, 2x9ArH), 8.18 (1H, s, CH=N) and 8.20 (1H, s, CH=N).

Compound 247

^{1}H N.M.R. δ(ppm) 1.1 (6H, d, CH_3CHCH_3), 1.15 (6H, d, CH_3CHCH_3), 2.41 (3H, s, CH_3S), 2.48 (3H, s, CH_3S), 2.60 (2H, m, $CH(CH_3)_2$x2), 3.85 (6H, s, CH_3Ox2), 4.05 (6H, s, 2xCH_3O_2C), 4.10 2H, s, CH_2Ar), 4.20 (2H, s, CH_2Ar), 7.0-7.5 (8H, m, 2x4ArH) and 7.52-7.61 (2H, m, CH=Nx2).

Compound 248

^{1}H N.M.R. δ(ppm) 1.28 (18H, s, $(CH_3)_3C$x2), 2.44 (3H, s, CH_3S), 2.56 (3H, s, CH_3S), 3.80 (3H, s, CH_3O), 3.85 (3H, s, CH_3O), 4.05 (3H, s, CH_3O_2C), 4.10 (3H, s, CH_3O_2C), 4.15 (2H, s, CH_2Ar), 4.24 (2H, s, CH_2Ar), 6.9-7.6 (24H, m, 2x12 ArH), 8.21 (1H, s, CH=N) and 4.23 (1H, s, CH=N).

Compound 249

^{1}H N.M.R. δ(ppm) 2.42 (3H, s, CH_3S), 2.56 (3H, s, CH_3S), 3.78 (3H, s, CH_3O), 3.82 (3H, s, CH_3O), 4.05 (3H, s, CH_3O_2C), 4.10 (3H, s, CH_3O_2C), 4.25 (2H, s, CH_2Ar), 4.30 (2H, s, CH_2Ar), 6.9-7.6 (24H, m, 2x12ArH), 8.24 (1H, s, CH=N) and 8.28 (1H, s, CH=N).

Compound 250

^{1}H N.M.R. δ(ppm) 0.90 (6H, m, CH_3CH_2x2), 1.36 (12H, m, $CH_3CH_2CH_2CH_2$x2), 1.45 (8H, m, CH_2CH_2Ox2), 2.44 (3H, s, CH_3S), 2.56 (3H, s, CH_3S), 3.84 (3H, s, CH_3O), 3.86 (3H, s, CH_3O), 4.0 (3H, s, CH_3O_2C), 4.16 (2H, s, CH_2Ar), 4.28 (2H, s, CH_2Ar), 6.8-7.6 (16H, m, 2x8ArH), 8.22 (1H, s, CH=N) and 8.24 (1H, s, CH=N).

Compound 251

^{1}H N.M.R. δ(ppm) 2.40 (3H, s, CH_3S), 2.50 (3H, s, CH_3S), 3.78 (3H, s, CH_3O), 3.84 (3H, s, CH_3O), 4.08 (3H, s, CH_3O_2C), 4.16 (3H, s, CH_3O_2C), 4.18 (2H, s, CH_2Ar), 4.30 (2H, s, CH_2Ar), 6.78-7.6 (22H, m, 2x11ArH), 8.26 (1H, s, CH=N) and 8.30 (1H, s, CH=N).

Compound 253

^{1}H N.M.R. δ(ppm) 2.44 (3H, s, CH_3S), 2.56 (3H, s, CH_3S), 3.80 (3H, s, CH_3O), 3.82 (3H, s, CH_3O), 4.02 (3H, s, CH_3O_2C), 4.04 (3H, s, CH_3O_2C), 4.18 (2H, s, CH_2Ar), 4.28 (2H, s, CH_2Ar), 5.7-6.1 (2H, t, CHF_2x2), 7.1-7.8 (16H, m, 2x8ArH), 8.32 (1H, s CH=N) and 8.34 (1H, s, CH=N).

Compound 254

^{1}H N.M.R. δ(ppm) 1.38 (3H, m, CH_3CH), 1.55 (6H, m, 2xCH_3CH), 2.42 (3H, s, CH_3S), 2.46 (3H, s, CH_3S), 2.50 (3H, s, CH_3S), 3.73 (3H, m, 3x$CHCH_3$), 3.80 (6H, m, 2xCH_3ON), 3.82 (3H, s, CH_3ON), 4.02 (6H, m, 2xCH_3OOC), 4.06 (3H, s, CH_3OOC), 4.10 (2H, s, CH_2Ar), 4.18 (2H, s, CH_2Ar), 4.24 (2H, s, CH_2Ar), 7.1 (3H, m, 3xArH), 7.26 (21H, m, 3x7ArH), 7.50 (3H, s, 3xArH) and 7.74 (3H, m, 3xN=CH).

Compound 255

^{1}H N.M.R. δ(ppm) 1.14-1.20 (24H, m, 4xCH(CH_3)$_2$), 2.38 (6H, s, 2xCH_3S), 2.42 (3H, s, CH_3S), 2.46 (3H, s, CH_3S), 3.22 (4H, m, 4xCH(CH_3)$_2$), 3.83 (12H, m, 4xCH_3ON), 4.02 (12H, m, 4xCH_3OOC), 4.08 (4H, m, 2xCH_2Ar), 4.22 (4H, m, 2xCH_2Ar), 7.12 (4H, m, 2xCH_2Ar), 7.12 (4H, m, 4xArH), 7.34 (8H, m, 4x2ArH), 7.48 (4H, m, 4xArH) and 7.65 (4H, m, 4xN=CH).

Compound 256

^{1}H N.M.R. δ(ppm) 2.42 (3H, s, CH_3S), 2.50 (3H, s, CH_3S), 3.80 (6H, m, 2xArOCH_3), 3.84 (6H, m, 2xCH_3ON), 4.04 (6H, m, 2xCH_3OOC), 4.14 (2H, s, CH_2Ar), 4.26 (2H, s, CH_2Ar), 6.88 (8H, m, 2xHC=CH and 2x2ArH), 7.14-7.58 (12H, m, 2x6ArH) and 8.14 (3H, m, 3xN=CH).

Compound 257

^{1}H N.M.R. δ(ppm) 2.40 (3H, s, CH_3S), 2.44 (3H, s, CH_3S), 2.44-2.76 (8H, m, 2x2CH_2), 3.66 (4H, m, 2xCH_2), 3.82 (4H, m, 2xCH_2), 3.82 (6H, m, 2xCH_3ON), 4.02 (3H, s, CH_3OOC), 4.04 (3H, s, CH_3OOC), 4.08 (2H, s, CH_2Ar), 4.18 (2H, s, CH_2Ar), 7.10 (2H, m, 2xArH), 7.34 (4H, m, 2x2ArH) and 7.50 (2H, m, 2xArH).

Compound 258

^{1}H N.M.R. δ(ppm) 0.88 (18H, m, 3x$(CH_2CH_3)_2$), 1.52 (12H, m, 3xCH$(CH_2CH_3)_2$, 2.18 (3H, m, 3xCH$(CH_2CH_3)_2$), 2.37 (3H, s, CH_3S), 2.40 (3H, s, CH_3S), 2.44 (3H, s, CH_3S), 3.84 (9H, m, 3xCH_3ON), 4.05 (9H, s, 3xCH_3OOC), 4.10 (2H, s, CH_2Ar), 4.20 (4H, m, 2xCH_2Ar), 7.12 (3H, m, Ar-H), 7.34 (6H, m, 3xArH), 7.48 (6H, m, 2xArH and 2xN=CH).

Compound 259

^{1}H N.M.R. δ(ppm) 1.06-2.06 (20H, m, 4x3CH and 4xCH_2), 2.40 (12H, m, 4xCH_3S), 2.83-3.10 (8H, m, 4xCH_2 bridging), 3.83 (12H, s, 4xCH_3ON), 4.02 (12H, m, 4xCH_3OOC), 4.18 (2H, s, CH_2Ar), 4.20 (6H, m, 3xCH_2Ar), 5.95-6.22 (8H, m, 4xCH=CH), 7.10 (4H, m, 4xArH), 7.36 (8H, m, 4x2ArH), 7.44 (4H, m, 4xArH) and 7.75 (4H, m, 4xN=CH).

Compound 260

^{1}H N.M.R. δ(ppm) 1.44 (6H, s, =C-C$(CH_3)_2$), 1.60 (3H, N=CCH_3), 1.64 (3H, s, N=CCH_3), 2.42 (3H, s, CH_3S), 2.48 (3H, s, CH_3S), 3.83 (6H, s, 2xCH_3ON), 4.02 (3H, s, CH_3OOC), 4.06 (3H, s, CH_3OOC), 4.14 (2H, s, CH_2Ar), 4.20 (2H, s, CH_2Ar) and 7.08-7.56 (16H, m, 2x8Ar-H).

Compound 261

^{1}H N.M.R. δ(ppm) 1.06 (6H, s, =CHC($\underline{CH_3}$)$_2$), 1.12 (6H, s, =CHC($\underline{CH_3}$)$_2$), 2.20 (4H, m, 2x$\underline{CH_2}$), 2.38 (3H, s, $\underline{CH_3}$S), 2.46 (3H, s, $\underline{CH_3}$S), 3.84 (6H, m, 2x$\underline{CH_3}$ON), 4.04 (6H, m, 2x$\underline{CH_3}$OOC), 4.10 (2H, s, $\underline{CH_2}$Ar), 4.18 (2H, s, $\underline{CH_2}$Ar), 5.02 (4H, m, 2xC=$\underline{CH_2}$), 5.60 (2H, m, 2x$\underline{CH}CH_2$), 7.10 (2H, m, 2xAr-$\underline{H}$), 7.32 (4H, m, 2x2Ar$\underline{H}$), 7.48 (2H, m, 2xAr$\underline{H}$), 7.55 (2H, m, 2xN=C$\underline{H}$).

Compound 262

^{1}H N.M.R. δ(ppm) 1.06 (12H, m, 4x$\underline{CH_3}$CH), 1.14 (12H, 4x$\underline{CH_3}$CH), 1.50-1.98 (8H, m, 4x$\underline{CH_2}$), 2.34 (4H, m, 4xCH$\underline{CH_3}$), 2.40 (6H, m, 2x$\underline{CH_3}$S), 2.44 (6H, m, 2x$\underline{CH_3}$S), 2.84 (4H, m, 4x$\underline{CH}CH_3$), 3.84 (12H, m, 4x$\underline{CH_3}$ON), 4.02 (12H, m, 4x$\underline{CH_3}$OOC), 4.08 (4H, m, $\underline{CH_2}$Ar), 4.20 (4H, m, 2x$\underline{CH_2}$Ar), 7.06-7.40 (32H, 4x8 Ar-$\underline{H}$) and 7.54 (4H, m, 2xAr$\underline{H}$ and 2xN=C$\underline{H}$).

Compound 263

^{1}H N.M.R. δ(ppm) 2.34 (12H, m, 2xN=C$\underline{CH_3}$ and 2xN=C$\underline{CH_3}$), 2.44 (3H, s, $\underline{CH_3}$S), 2.58 (3H, s, $\underline{CH_3}$S), 3.80 (3H, s, $\underline{CH_3}$ON), 3.88 (3H, s, $\underline{CH_3}$ON), 4.04 (6H, m, 2x$\underline{CH_3}$OOC), 4.15 (2H, s, $\underline{CH_2}$Ar), 4.30 (2H, s, $\underline{CH_2}$Ar), 7.10-7.40 (10H, m, 2x5Ar$\underline{H}$), 7.55 (2H, m, 2xAr$\underline{H}$) and 7.66 (4H, m, 2x2Ar$\underline{H}$).

Compound 264

^{1}H N.M.R. δ(ppm) 2.45 (3H, s, S$\underline{CH_3}$), 2.55 (3H, s, S$\underline{CH_3}$), 3.85 (3H, s, $\underline{CH_3}$ON), 3.90 (3H, s, $\underline{CH_3}$ON), 4.10 (6H, m, $\underline{CH_3}$OOC), 4.15 (2H, m, Ar-C$\underline{H_2}$), 4.30 (2H, s, Ar-C$\underline{H_2}$), 6.95-7.10 (8H, m, Ar-$\underline{H}$), 7.15-7.20 (4H, m, Ar-$\underline{H}$), 7.35-7.40 (8H, m, Ar-$\underline{H}$), 7.55 (2H, m, Ar-$\underline{H}$), 7.70-7.80 (4H, m, Ar-$\underline{H}$), 8.30 (1H, s, N=$\underline{CH}$) and 8.35 (1H, s, N=$\underline{CH}$).

Compound 265

^{1}H N.M.R. δ(ppm) 2.45 (3H, s, SCH$_3$), 2.55 (3H, s, SCH$_3$), 2.65 (3H, s, SCH$_3$), 3.85 (3H, s, CH$_3$ON), 3.90 (6H, s, CH$_3$ON), 4.00 (9H, m, NCH$_3$), 4.10 (9H, m, CH$_3$OOC), 4.30 (6H, m, ArCH$_2$), 6.20 (3H, m, Het-H), 6.60 (3H, m, Het-H), 6.80 (3H, m, Het-H), 7.25 (3H, m, Ar-H), 7.30-7.45 (6H, m, Ar-H), 7.60 (3H, m, Ar-H) and 8.30 (3H, m, N=CH).

Compound 266

^{1}H N.M.R. δ(ppm) 2.45 (3H, s, =CCH$_3$), 2.55-2.70 (9H, m, =CCH$_3$and 2xCH$_3$S), 3.85 (3H, s, CH$_3$ON), 3.90 (3H, s, CH$_3$ON), 4.08 (6H, m, 2xCH$_3$OOC), 4.15 (2H, s, CH$_2$Ar), 4.34 (2H, s, CH$_2$Ar), 7.12-8.00 (14H, m, 2x4ArH and 2x3Het-H), 8.35 (1H, s, N=CH) and 8.40 (1H, s, N=CH).

Compound 267

^{1}H N.M.R. δ(ppm) 2.44 (9H, s, 3xCCH$_3$), 2.54 (3H, s, CH$_3$S), 2.66 (3H, s, CH$_3$S), 2.76 (3H, s, CH$_3$S), 3.96 (9H, m, 3xCH$_3$ON), 4.08 (9H, m, 3xCH$_3$OOC), 4.30 (2H, s, CH$_2$Ar), 4.34 (2H, s, CH$_2$Ar), 4.55 (2H, s, CH$_2$Ar) and 7.00-7.62 (21H, m, 3x4Ar-H and 3x3Het-H).

Compound 272

^{1}H N.M.R. δ(ppm) 2.44 (3H, s, CH$_3$S), 2.56 (3H, s, CH$_3$S), 3.82 (3H, s, CH$_3$ON), 3.86 (3H, s, CH$_3$ON), 4.06 (6H, m, 2xCH$_3$OOC), 4.18 (2H, s, CH$_2$Ar), 4.30 (2H, s, CH$_2$Ar), 7.15-8.04 (14H, m, 2x7Ar-H), 8.28 (1H, s, N=CH) and 8.30 (1H, s, N=CH).

Test Example

Compounds were assessed for activity against one or more of the following:

Erysiphe graminis f sp. tritici: wheat powdery mildew
Pyricularia oryzae: rice blast
Leptosphaeria nodorum: glume blotch
Phytophthora infestans: late blight of potatoes
Plasmopara viticola: downy mildew of vines

Aqueous solutions or dispersions of the compounds at the desired concentration, including a wetting agent, were applied by spray or by drenching the stem base of the test plants, as appropriate. After a given time, plants or plant parts were inoculated with appropriate test pathogens and kept under controlled environmental conditions suitable for maintaining plant growth and development of the disease. After an appropriate time, the degree of infection of the affected part of the plant was visually estimated. Compounds are assessed on a score of 1 to 3 where 1 is little or no control, 2 is moderate control and 3 is good to total control. At a concentration of 500 ppm (w/v) or less, the following compounds scored 2 or more against the fungi specified.

Erysiphe graminis f sp. tritici

1, 3, 5, 11, 14, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 32, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 62, 69, 70, *74,* 76, 77, 78, 79, 80, 81, 89, 91, 94, 95, 96, 97, 98, 99, 103, 104, 112, 113, 114, 115, 116, 117, 123, 126, 127, 129, 130, 131, 132, 134, 135, 139, 140, 141, 142, 143, 144, 145, 146, 147, 150, 151, 167, 176, 177, 178, 183, 184, 189, 190, 212, 214, 215, 217, 219, 220, 243, 245, 249, 255, 260 and 261.

Pyricularia oryzae

1, 2, 3, 4, 5, 6, 9, 11, 12, 17, 18, 20, 21, 22, 23, 24, 25, 27, 30, 32, 38, 39, 42, 44, 45, 46, 48, 49, 52, 62, 63, 64, 65, 66, 67, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 91, 92, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 155, 156, 157, 158, 159, 161, 163, 164,

165, 167, 169, 170, 171, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 188, 189, 191, 192, 193, 194, 195, 197, 199, 200, 202, 203, 218, 219, 220, 221, 222, 224, 225, 243, 245, 249, 254, 255, 258, 260 and 261.

Leptosphaeria nodorum

1, 3, 4, 5, 6, 11, 17, 18, 19, 20, 22, 23, 24, 25, 29, 32, 38, 39, 42, 43, 44, 49, 62, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 101, 102, 104, 105, 107, 108, 112, 113, 114, 115, 116, 117, 119, 120, 122, 123, 124, 125, 126, 127, 129, 130, 131, 132, 139, 140, 141, 142, 143, 144, 145, 146, 147, 150, 151, 176, 177, 178, 183, 184, 188, 189, 192, 194, 200, 203, 218, 219, 220, 221, 222, 224, 225, 243, 245, 249, 254, 255, 258, 260 and 261.

Phytophthora infestans

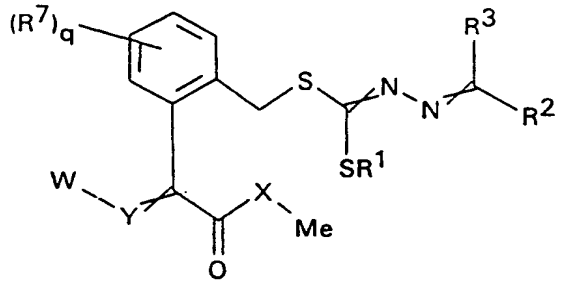
6, 9, 10, 11, 14, 15, 16, 22, 28, 69, 70, 71, 72, 74, 76, 77, 78, 79, 80, 81, 88, 91, 95, 96, 97, 98, 99, 113, 114, 115, 116, 117, 119, 123, 124, 127, 129, 130, 131, 132, 134, 135, 139, 140, 141, 142, 143, 144, 145, 147, 150, 151, 155, 156, 157, 159, 163, 165, 166, 169, 170, 174, 176, 177, 178, 184, 214, 219, 223, 236, 237, 238, 245, 247, 254, 255, 258, 259, 261, 265 and 266.

Plasmopara viticola

2, 4, 6, 8, 9, 10, 11, 12, 14, 16, 18, 21, 22, 29, 31, 33, 34, 35, 36, 43, 44, 45, 48, 49, 50, 52, 62, 64, 66, 67, 68, 69, 70, 72, 74, 76, 77, 78, 79, 80, 81, 84, 85, 86, 87, 90, 91, 91, 92, 93, 94, 95, 96, 98, 99, 101, 102, 104, 105, 106, 107, 108, 109, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 124, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 182, 183, 184, 185, 202, 206, 211, 212, 213, 214, 215, 216, 220, 235, 236, 237, 238, 240, 241, 246, 247, 249, 252, 259, 261 and 265.

CLAIMS

1 The invention provides a compound of general formula I



(I)

wherein

X is O or NH;

Y is CH or N;

W is methyl or methoxy;

R^1 and R^2, which may be the same or different, are optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted cycloalkyl, optionally substituted cycloalkenyl, optionally substituted phenyl or optionally substituted heterocyclyl;

R^3 has the same meaning as R^2 or can be hydrogen; or

R^2 and R^3 together with the carbon to which they are attached form a 5- to 7-membered heterocyclyl, cycloalkyl or cycloalkenyl group which is optionally substituted;

R^7 is alkyl, haloalkyl, alkenyl, alkynyl, cycloalkyl, halogen, cyano, alkoxy, alkylthio, haloalkoxy, and optionally substituted phenyl; and

q is 0 to 4.

2 A compound according to claim 1 wherein the double bond attached to Y is of E geometry.

3 A compound according to claim 1 or 2 wherein R^1 is optionally substituted alkyl.

4 A compound according to claim 3 where R^1 is methyl.

5 A compound according to any preceding claim wherein R^3 is hydrogen.

6 A compound according to any preceding claim wherein q is 0.

7 A compound according to any preceding claim wherein R^2 is optionally substituted alkyl, optionally substituted phenyl or optionally substituted heterocyclyl.

8 A compound according to claims 7 wherein when R^2 is optionally substituted branched alkyl.

9 A compound according to claim 8 wherein R^2 is optionally substituted tertiary butyl.

10 A compound according to claim 7 wherein when R^2 is a phenyl group substituted by one or more electron-withdrawing groups.

11 A compound according to claim 10 wherein the electron with drawing group or groups are halogen.

12 A compound according to claim 7 wherein when R^2 is optionally substituted heterocyclyl, the heterocyclyl group is aromatic and deactivating.

13 A compound according to claim 12 wherein the heterocyclyl group is optionally substituted pyridine or pyrimidine.

14 A compound according to any preceding claim wherein X is NH, Y is N and W is methoxy.

15 A pesticidal composition comprising compounds as claimed in any preceding claim in admixture with an agriculturally acceptable diluent or carrier.

INTERNATIONAL SEARCH REPORT

Inte nal Application No
PCT 98/01234

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C337/04 C07D213/53 C07D333/22 C07D307/52 C07D213/61
C07D333/28 C07D207/32 C07D215/12 C07D271/06 A01N47/42

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 299 694 A (SCHERING AGROCHEMICALS) 18 January 1989 cited in the application see the whole document	1,15
A	DE 44 39 334 A (BAYER) 9 May 1996 see the whole document	1,15

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 July 1998	04/08/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	English, R

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

[redacted]ion on patent family members

[redacted]/GB 98/01234

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0299694 A	18-01-1989	AU 607235 B	28-02-1991
		CN 1031227 A,B	22-02-1989
		DK 381588 A	12-01-1989
		FI 883297 A,B,	12-01-1989
		IL 87020 A	12-09-1996
		JP 1031746 A	02-02-1989
		JP 2688495 B	10-12-1997
		KR 9612207 B	16-09-1996
		PT 87938 A,B	30-06-1989
		US 5304530 A	19-04-1994
		US 5192357 A	09-03-1993
DE 4439334 A	09-05-1996	AU 3806495 A	31-05-1996
		WO 9614295 A	17-05-1996